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NUMBER 3

AN ATTEMPT TO DETECT THE PRESENCE OF METASTABLE ATOMS IN ACTIVE NITROGEN BY LIGHT ABSORPTION¹

BY W. S. HERBERT,² G. HERZBERG³ AND G. A. MILLS⁴

Abstract

In order to explain the nitrogen afterglow, Cario and Kaplan have assumed the presence of metastable 2D and 2P atoms in active nitrogen. The nitrogen emission lines at 1492\AA and 1742\AA have these metastable states as lower states, and should therefore be absorbed by active nitrogen. However, no absorption has been found by the writers. This leads to $1/6000\%$ as an upper limit for the stationary concentration of metastable atoms in active nitrogen, which is compatible with the experiments. In order to account for the observed intensity of the afterglow, on the basis of Cario-Kaplan's theory, a lifetime of the metastable 2P atoms $\leq 8 \times 10^{-4}$ sec. has to be assumed and a concentration of metastable molecules greater than $1/330\%$.

Introduction

According to the theory put forward by Cario and Kaplan (1), active afterglowing nitrogen contains, besides normal nitrogen atoms in the 4S state, also nitrogen atoms in the metastable 2D and 2P states, 2.37 and 3.54 volts respectively above the 4S groundstate, and metastable nitrogen molecules in the $A^3\Sigma$ state. The excitation of the visible afterglow bands in particular (upper state $B^3\Pi_u$) according to Cario and Kaplan is due to the collision of a nitrogen $A^3\Sigma$ molecule with a 2P nitrogen atom. In fact the energy of the highest vibrational state excited in the production of the afterglow bands agrees very nearly with the energy of a nitrogen molecule ($A^3\Sigma$) + a nitrogen atom (2P). If this explanation is correct, one would expect a certain stationary concentration of 2P nitrogen atoms in nitrogen that shows the afterglow. Indeed, Jackson and Broadway (4), a number of years ago, found the presence of 2P nitrogen atoms in a Stern-Gerlach experiment with a molecular beam taken from active nitrogen. It seemed puzzling, however, that they observed only the $^2P_{3/2}$ component of the 2P term and not the $^2P_{1/2}$ component, and that there was no indication of the 4S state. The writers therefore thought it worthwhile to try to find evidence for the presence of the metastable atoms by an entirely different method, namely, by the absorption of light from the metastable states.

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Experimental

The lines of longest wave-length that can be absorbed by the ^2P and ^2D states are the doublet at 1742\AA and the doublet at 1492\AA , respectively. Thus a vacuum spectrograph had to be used. If a continuous spectrum is used as a background for the absorption experiments, rather high resolution has to be used in order to observe narrow and faint absorption lines (3). Instead the writers used the emission lines of nitrogen as a background because the only spectrograph available to them was a small Cario-Schmidt-Ott. Evidently the sensitivity of the test does then not depend on the dispersion of the spectrograph. The emission lines of N I were produced in a powerful uncondensed discharge through nitrogen. After the tube was operated for a while the nitrogen lines came out very strongly in emission, and could be photographed within a few minutes when the distance between the discharge tube and the slit of the spectrograph was 60 cm.

The afterglowing nitrogen was pumped from a condensed discharge, at a pressure of about 6 mm., through the absorption tube of 60 cm. length and 8 mm. diameter placed between the spectrograph and the background discharge tube. Thin crystalline quartz windows, transparent to 1450\AA , were used to separate the absorption tube from the spectrograph and the light source. The exciting discharge of the active nitrogen was as near as possible to the absorption tube and the intensity of the afterglow for at least 10 to 20 cm. of the absorption tube was so great that its spectrum appeared on the plates for exposure times of only 10 min. (aperture of spectrograph, 1 : 10).

Results and Discussion

No difference in the intensities of the nitrogen doublets at 1742\AA and 1492\AA could be detected between exposures taken when the nitrogen passing through the absorption tube was activated and when it was not. That is, *no absorption of these lines was found*. This does not necessarily mean that there are no metastable atoms in active nitrogen, but it does prove that if they are present their concentration must be low. It is possible to deduce an upper limit to this concentration for the experimental arrangement used.

It seems safe to assume that the f -value (number of dispersion electrons) for the lines 1742\AA ($2p^2\text{P}-3s^2\text{P}$) and 1492\AA ($2p^2\text{D}-3s^2\text{P}$) is of the order 0.1, the transition being entirely allowed and involving low values of the principal quantum number only. Therefore, it follows that the absorption coefficient for the centre of the line at atmospheric pressure (6) is of the order, $k_a^{760} = 10^7$. Since the intensity of the afterglow decreased appreciably along the absorption tube of 60 cm. length, an absorbing length of only 10 cm. was assumed. It can be stated with certainty that a 50% decrease of intensity of the nitrogen emission lines would have been observed. It follows that the absorption coefficient k_a^p for the actual partial pressure of nitrogen ^2P and ^2D atoms, respectively, must have been smaller than 0.16. In deriving this value, consideration was given to the fact that the emission and the absorption

lines have different Doppler widths, owing to the difference in the temperatures involved (5, p. 1021). The ratio $\frac{k_o^p}{k_o^{760}}$ gives the maximum partial pressure of ^2D and ^2P atoms that is compatible with the observed fact that no absorption by these states was noticeable. This upper limit is 1×10^{-5} mm. or 4×10^{11} $^2\text{P}(^2\text{D})$ atoms per cc.

Experiments by Wrede (7, p. 65) and others have shown that active nitrogen produced in the ordinary way contains about 1% atoms. This corresponds to a partial pressure of 0.06 mm. in the present experiments. Thus it is seen that the ^2P and ^2D atoms, if present at all, form only a minute fraction, less than 1/6000, of the atomic part of active nitrogen.

By comparison with a calibrated mercury arc the number of quanta emitted in the green, yellow and red by active nitrogen was determined roughly. The writers found 5×10^{14} quanta per cc. per sec. Since according to Kaplan and Cario's theory every quantum of the *visible* afterglow bands is emitted by the action of one ^2P atom, it follows that the stationary concentration on the basis of this theory in the experiment must have been larger than $5 \times 10^{14} \tau$ per cc., where τ is the average lifetime of a ^2P atom. But (see above) the negative result of the absorption experiments shows that the number of ^2P atoms is smaller than 4×10^{11} atoms per cc., hence it follows that

$$\tau \leq 8 \times 10^{-4} \text{ sec.}$$

A lower limit for the number of $\text{A}^3\Sigma$ molecules may be derived (assuming that there is no abnormal collision radius) if the limitation of the lifetime is due entirely to collisions with $\text{A}^3\Sigma$ molecules and subsequent production of the visible afterglow. A value 6.5×10^{12} atoms per cc. (1.8×10^{-4} mm.) is obtained. This value is about 16 times larger than the maximum number of ^2P atoms which is compatible with the writers' experiments but about 330 times smaller than the number of normal atoms. It should be noted that the number of $\text{A}^3\Sigma$ molecules is derived on the assumption that Cario and Kaplan's theory is correct, whereas the upper limit for the number of ^2P atoms derived is independent of this assumption.

Thus, of active nitrogen 1% is normal atoms, less than 1/6000% is metastable atoms and, if the Cario-Kaplan theory is right, 1/330% or more is metastable $\text{A}^3\Sigma$ molecules. As is seen, the unexpectedly low concentration of metastable atoms as found in these experiments does not necessarily contradict the Cario-Kaplan theory if there is a suitable concentration of metastable $\text{A}^3\Sigma$ molecules. Yet the concentration of the metastable molecules can be so low that it will be practically impossible to prove their presence by absorption experiments.* It should be easy, however, to detect the presence of normal atoms by absorption if it were not for the fact that the resonance lines lie at 1190\AA , which makes the experiment impossible for the fluorite spectrograph used.

*Frost and Oldenberg (2) were unable to find absorption by metastable molecules in a discharge which they thought has a greater concentration of metastable molecules than active nitrogen.

The results obtained are evidently in disagreement with the Stern-Gerlach experiment by Jackson and Broadway (4) because, according to the above, normal ^{4}S atoms constitute by far the largest part of active nitrogen and they would give quite a different Stern-Gerlach pattern from that observed by Jackson and Broadway. The possibility that their method of detection was sensitive only to ^2P atoms and not to ^4S atoms seems rather remote, and the difficulty that they observed only $^2\text{P}_{\frac{1}{2}}$ atoms and no $^2\text{P}_{\frac{3}{2}}$ atoms would even then remain.

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ABSORPTION CURVES AND RANGES FOR HOMOGENEOUS β -RAYS¹

By J. S. MARSHALL² AND A. G. WARD³

Abstract

β -rays were bent in a uniform magnetic field, after which they entered, as approximately homogeneous rays, an ionization chamber connected to a linear amplifier. Absorption curves in aluminium were determined for various values of $H\rho$. The active materials were radium *E* and uranium *X*.

Apparatus

The β -ray spectrometer consisted of an evacuated brass box, 22 by 14 by 4 cm., placed between the poles of an electromagnet that practically gave a uniform field over the path of the β -rays in the box. Two slits were used, one to define the angular width of the beam, the other to reduce scattered radiation from the walls of the box, this scattered radiation being further reduced by lining the walls with cardboard. Both slits limited the beam to a width of 1 cm. in planes parallel to the direction of the magnetic field. The window of the spectrometer was 10 by 5 mm. It was covered with one layer of ordinary cellophane of 0.00318 gm. per sq. cm. β -rays that emerged from the spectrometer possessed radii of curvature varying from 6.80 to 7.20 cm., the average radius being 7.00 cm. In most of the experiments, the window of the ionization chamber was 7 cm. distant from the window of the spectrometer. The strengths of the magnetic field could be measured with an error less than $\frac{1}{4}$ of 1%. The value of ρ taken is correct to $\frac{1}{3}$ of 1%.

The ionization chamber was made of steel, 14 cm. inner diameter and 13 cm. deep. It was filled with carbon dioxide at atmospheric pressure. The window was covered with two layers of cellophane, the outer layer waterproof, the inner layer ordinary cellophane coated with drawing ink to make it conducting. The mass per square centimetre of the window was 0.00690 gm. Ionization currents could be measured accurately to 2×10^{-16} amp. by means of an F.P. 54 plotron in an amplifying circuit devised by DuBridge and Brown (2).

Results

Some typical absorption curves are shown in Fig. 1, allowance being made for the materials the β -rays had to pass through from the spectrometer to the ionization chamber. Each curve is initially concave towards the axis of abscissas, the linear part is fairly well defined and there is quite an appreciable tail on the curve. The linear part of each curve has been extended so as to cut the axis of abscissas, and the point where it cuts the axis has been called the extrapolated range in gm. per sq. cm. of aluminium for β -rays of

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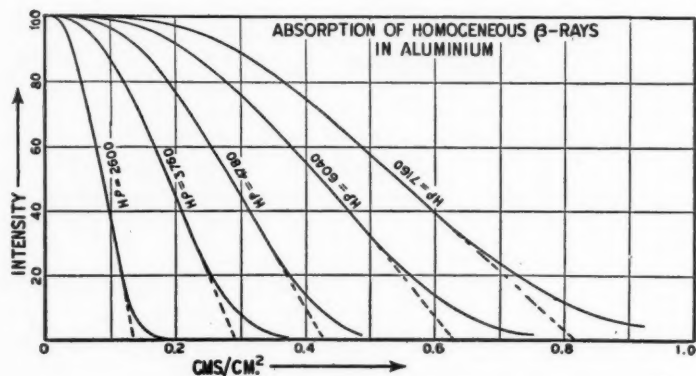


FIG. 1.

the given $H\rho$. It is customary to do this, but it cannot really be justified, the real range being considerably greater as can be seen when one considers the narrow range in $H\rho$ for each beam, *viz.*: from 6.8 to 7.2 H and the appreciable tail on each absorption curve.

The ranges determined in the manner described above have been plotted against $H\rho$ (Figs. 2 and 3). Schonland (5), Varder (6), Madgwick (4) and Eddy (3) have determined similar ranges for β -rays in aluminium and, for

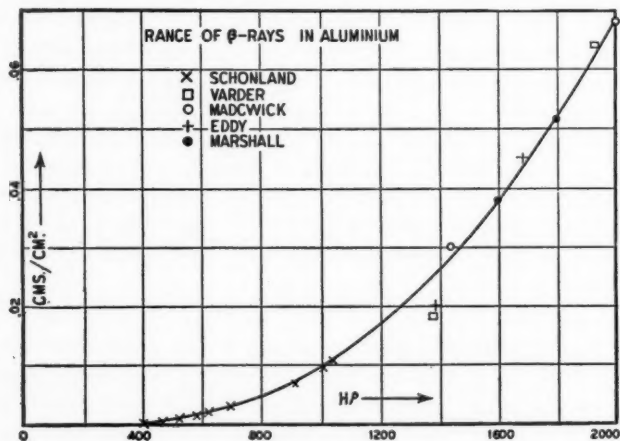


FIG. 2.

the sake of completeness, their results are also given. It will be noticed that our results lie midway between those of other experimenters. The initial portions of the curves obtained by us correspond to those on similar curves obtained by Crowther (1) and Wilson (7), but differ markedly from those obtained by Varder and Madgwick. This is due, no doubt, to differences in

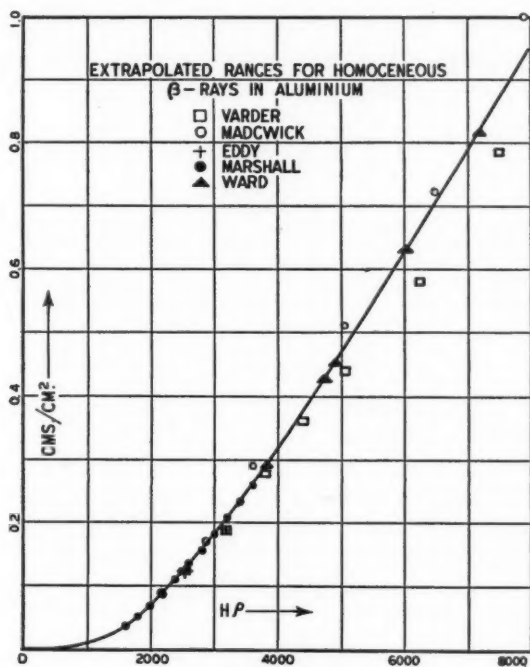


FIG. 3.

the experimental conditions, but it is felt that curves such as those given in Fig. 1 correspond more closely to what actually happens and they are certainly more useful to other experimenters.

Acknowledgment

The authors wish to thank Dr. J. A. Gray for the interest he has taken in this work.

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THE END POINTS OF THE β -RAY SPECTRA OF RADIUM *E* AND URANIUM X_2 ¹

By A. G. WARD² AND J. A. GRAY³

Abstract

The end points of the β -ray spectra of radium *E* and uranium X_2 have been measured, using semi-circular magnetic focusing and an ionization chamber connected to a linear amplifier. Experimental results give end points of $H\rho = 5250$ gauss-cm. for radium *E* and $H\rho = 9300$ gauss-cm. for uranium X_2 .

Introduction

It was shown indirectly by Gray (2) in 1913 that the β -rays of radium *E* should have a definite end point. He found that when these β -rays were absorbed by paper, after a while, they became more and more absorbable, showing that they had a definite range. A magnetic field was used to distinguish between β - and γ -rays. As he pointed out then, a similar result could be deduced from earlier experiments by Schmidt (7). The fact that there is a definite range is shown even more clearly by the later experiments of Gray and Henderson (3).

Experimental

For some time the writers have been observing the properties of β -rays scattered through large angles by thin metallic foils, and to aid in the interpretation of these experiments it has been found necessary to determine the distribution of β -rays in the spectra of the active materials used, radium *E* and uranium X_2 . While the writers were obtaining these spectra, it was thought worth while to measure the end point, or maximum value of the energy or momentum ($H\rho$) of these β -rays, as accurately as possible. The apparatus that was used was exactly the same as that described by Marshall and Ward (6). The results for radium *E* (radium *D* was used as a source) are shown in Fig. 1, in which the ionization obtained with a definite value of magnet current is plotted against that current. It will be noted that in each graph there are two curves, the lower curve indicating the intensity when an aluminium absorption sheet, 0.175 gm. per sq. cm., was placed in front of the ionization chamber. This was done so that one could distinguish clearly between scattered radiation and radiation that was due to the bending of the rays in the magnetic field. Near the end point, this absorption sheet reduces the intensity of the radiation to 80% of its initial value.

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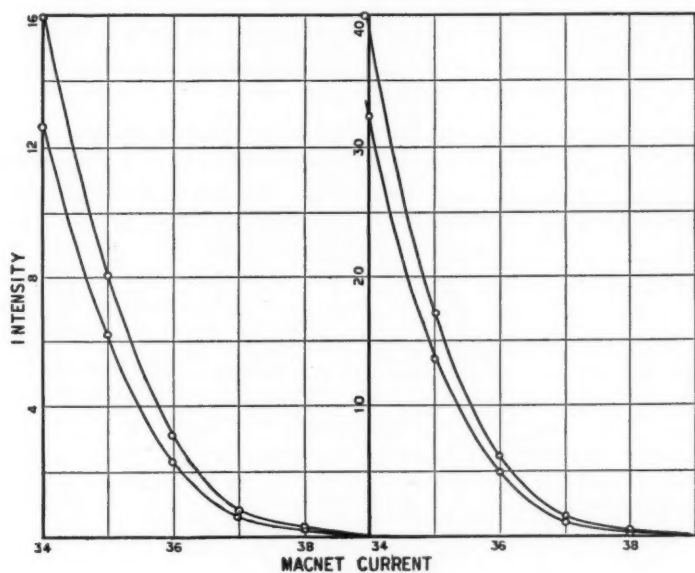


FIG. 1.

Results

The first graph shows the results obtained when the slit limiting the angular width of the beam in the spectrometer was $\frac{1}{2}$ in. wide, the second when the same slit was 1 in. wide and the spectrometer somewhat nearer the ionization chamber. As a result the intensities in the latter case are about two and one-half times as great as in the former, except for the larger values of the current. In the first case the radii of curvature of β -rays emerging from the spectrometer varied from 6.80 to 7.20 cm., in the second case from 6.80 to 7.30 cm.

In neither case could the writers find any intensity with a current of 0.39 amp. ($H = 772$ gauss), but in each case a definite intensity was obtained with a current of 0.38 amp. ($H = 759$ gauss). However, in each case with the latter current the intensities were, as far as could be determined by the writers, the same. If there were a real tail to the curve, this would not be true so that the apparent tail shown in both cases is due entirely to the finite width of the defining slits in the spectrometer. This appears to cut the axis of abscissas in the neighborhood of 0.39 amp. which corresponds to a field strength of 772 gauss, giving an end point at 6.8 cm. $\times 772$ gauss or at $H\rho = 5250$ gauss-cm. which should be correct to 1%.

It will be realized that an apparent tail will be obtained only when the source is sufficiently strong. In an actual experiment using a source of

1/40 the intensity, the writers did not obtain such a tail, but found that if the average instead of the minimum radius of curvature was used, the same value for the end point was obtained. In this way the writers found an end point for uranium X_2 at $H\rho = 9300$ gauss-cm.

The writers' value for the end point of radium E is in fair agreement with the values reported by Madgwick (5), Alichanow, Alichanian and Dzelepov (1) and by Lyman (4), who obtained values of 5000, 5200, and 5280 gauss-cm. respectively. Of these experimenters, Lyman took the most care to determine the end point accurately, but it should be mentioned that none of them took the care the writers did to show that the tail at the end of the spectrum is due entirely to the finite range of radii of curvature permitted by the spectrometer.

The results of the writers' experiments on radium E were reported at the annual meeting of the Royal Society of Canada in May, 1936.

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THE SCATTERING OF X-RAYS AT VERY SMALL ANGLES¹

BY H. H. PENLEY² AND J. A. GRAY³

Abstract

The scattering of X-rays at small angles (minutes of arc) in commercial samples of charcoal and powdered graphite and in anthracene precipitate was investigated. In addition, the effect of pressure on the scattering in Shawinigan charcoal was determined. An absorption method, which is described, was used and the results are shown graphically in the accompanying figure.

Apparatus

A shielded filament tube of the type described by Dershem (3) was used as a source of X-rays. The target was made of copper. The rays emerged horizontally through a nickel window 0.001 in. thick. The beam was collimated by two narrow vertical platinum slits 7 cm. apart. A third slit was mounted vertically, in such a way that both its width and position on a horizontal line perpendicular to the X-ray beam could be independently adjusted. The scattering cell was placed in the collimated beam close to the second slit. For the measurements of X-ray intensity a shielded Geiger-Müller tube counter with an aluminium window was used, and this was placed just behind the third slit. The impulses were amplified and then recorded by means of a scale-of-two thyatron circuit with impulse counter. The high voltage supply was obtained from a rectifier circuit with a voltage stabilizer of the type described by Street and Johnson (9).

Discussion and Results

The apparent mass absorption coefficient, $\frac{\mu}{\rho}$, was obtained in the usual way from the equation $I = I_0 e^{-\frac{\mu}{\rho} m}$, where I_0 is the initial number of counts, I the count after the X-rays passed through the scattering material of mass m per sq. cm. The third slit was placed so that its centre coincided with that of the primary beam and for the different widths of it at which measurements were made, the angle that it subtended at the scattering material was calculated, half this angle being taken as the maximum angle of scattering of the scattered rays entering the counter. This can be only approximate for the smaller widths of the third slit owing to the finite width of the primary beam. In Fig. 1 this particular angle of scattering has been called the scattering angle and has been plotted as ordinate, μ/ρ as abscissa. It will be noticed that μ/ρ decreases as the scattering angle increases, because more scattered radiation enters the counter as the third slit is increased in width. Ultimately

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μ/ρ tends to approach its true or normal value, μ_0/ρ , say. The difference $\mu/\rho - \mu_0/\rho$ may be then taken as some measure of the intensity of the radiation scattered between the angle given on the graph and large angles. In the experiments, it was found difficult to measure μ_0/ρ accurately, as in all cases I/I_0 was about 0.77, so that a small error in the determination of this ratio meant a much larger error in the calculated value of the absorption coefficient.

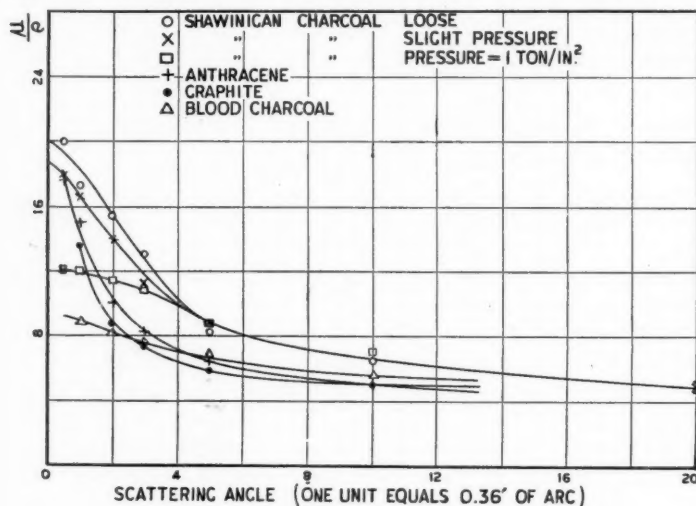


FIG. 1.

The scattering of X-rays in graphite and charcoal at small angles was reported by Gray and Zinn (5) and their work was continued in this laboratory by W. E. Bennett, who showed that there were two distinct types of scattering at small angles, one typical of charcoals and the other typical of precipitated anthracene. He showed that charcoals behave like gases of very high molecular weight, and he partially accounted for his results by a theory modelled after one given by Debye (2). He showed further that the second type of scattering could be partially explained by von Nardroff's (7) theory of the refraction and reflection of X-rays passing the small particles of the powder. Experiments on the scattering of X-rays by powders have also been carried out by Slack (8) and by Davis (1) and on charcoals by Krishnamurti (6).

The writers have tried to distinguish between the two types of scattering in these experiments. In the case of what might be called the von Nardroff scattering, the value of μ/ρ should tend to infinity as the maximum scattering angle approaches zero. This is not practicable as it would need a primary beam of zero width. If a gas is used as a scattering medium, $\frac{\mu}{\rho}$ tends to a maximum as the scattering angle approaches zero.

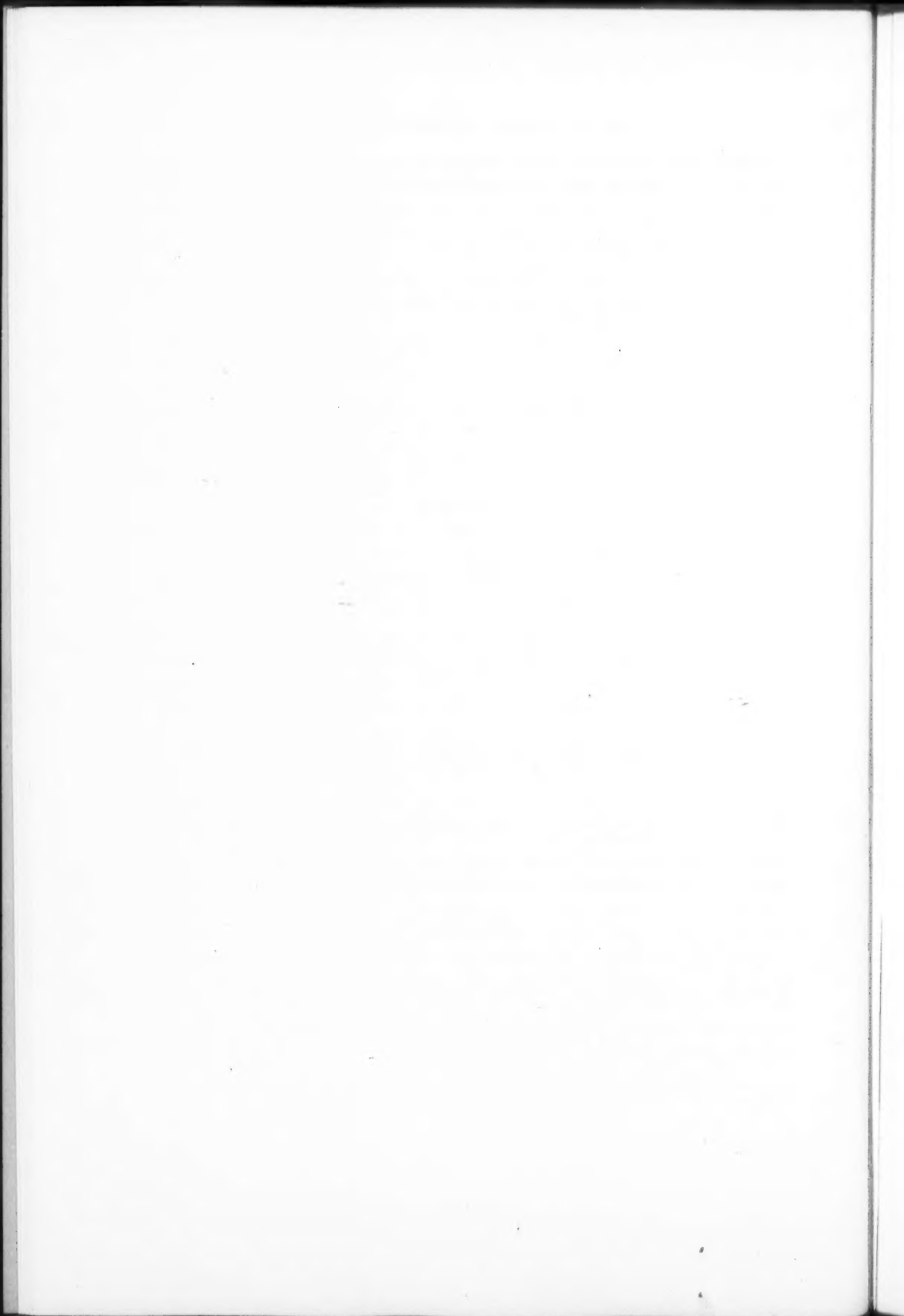
The writers' experiments confirm and extend the results of Bennett for they do show very clearly the distinction between the two types of scattering, the values of $\frac{\mu}{\rho}$ for the anthracene and graphite powder increasing markedly as the scattering angle is decreased, whereas in the charcoals $\frac{\mu}{\rho}$ does tend to increase to a maximum value. Using the Debye theory as modified by Bennett, the writers obtained a value of the order of 20 Å for the diameter of the smallest particles in the blood charcoal used, a value in agreement with that obtained by Krishnamurti (6), who used an entirely different but less exact method of dealing with the experimental results. In the Shawinigan charcoal most of the particles must be much larger. An average dimension of the particles in the anthracene precipitate that was formed by the addition of water to a solution of anthracene in ethyl alcohol and subsequent separation and drying of the precipitate was determined by use of a microscope and found to be 0.005 cm.

Three of the curves show the effect of pressure on scattering by Shawinigan charcoal at small angles. It will be noticed that the scattering at very small angles is markedly reduced by the application of pressure, but for angles greater than four minutes of arc there is no detectable change. According to theory, there should be no change in the scattering with the application of pressure if the particles are merely pushed together, while still retaining their random distribution, so that the decrease may be due to interference caused by a decrease in the randomness of the distribution or it may be due to the larger particles being broken down into smaller ones. When the particles are larger, μ/ρ is larger for zero angle of scattering and becomes equal to μ_0/ρ at a smaller angle of scattering. If one assumes it to be due entirely to the former cause, it is difficult to understand why there should be no change in the values of μ/ρ for scattering angles greater than two minutes of arc.

These experiments are being continued and it is believed that when completed they will give us further insight into the structure of substances like charcoal and artificial graphite. A full account will then be given of the work done in this laboratory by Zinn, Bennett and the writers. A brief account of the work by Bennett has been given in a note by Gray (4).

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THE INFLUENCE OF PENETRATION IN THE ALKALINE DELIGNIFICATION OF WOOD¹

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Abstract

The effect of various factors that might possibly influence the penetration of soda liquor into spruce wood has been examined. It was found that the rate of delignification was the same irrespective of the size of the sample, from a wood-meal of 0.005 mm. particle size up to a limiting chip thickness of about 10 mm. The density of the wood had no influence on the delignification other than that which would be expected from the higher original lignin content of the more dense wood. The presence of moisture in the chips was without result other than that of diluting the liquor, and the addition of wetting agents for facilitating the penetration rate was without significant effect.

Introduction

The digestion of wood in aqueous alkaline solution has long been an important process for the commercial preparation of cellulose pulp. Investigations of the mechanism of this process have been made from time to time, but no satisfactory explanation has yet been given for the complete reaction. From the chemical point of view, the process consists essentially in the formation of a water-soluble alkali-lignin compound, the cellulose being only slightly affected. The exact physico-chemical nature of this process is unknown. The manner in which such variables as concentration of the alkali, temperature, rate of penetration of the liquor, size and moisture content of the chip, etc., affect the rate of the delignification process, has never been the subject of an exhaustive survey in which all these factors were considered at the same time.

Macklin and Maass (3) developed a suitable experimental procedure for carrying out cooking experiments on a small scale under closely controlled and reproducible conditions, and they paid special attention to the delignification of spruce wood with sodium hydroxide solutions of high concentration. Their experimental technique was adopted in the present investigation, which was primarily concerned with an examination of those purely physical factors, such as size and shape of the wood chip, method of liquor penetration into the wood during the cooking process, density and moisture content of the wood, etc., that might affect the delignification process by influencing the rate of penetration of the active chemicals into the wood.

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The role played by the alkali, and the probable kinetics of the process will be considered in a subsequent paper. A further paper will discuss some observations on the quality and strength of pulps prepared under special experimental conditions. This may be of interest in the commercial application of the alkaline pulping process.

Experimental Procedure

The method employed consisted in carrying out small-scale pulping experiments with specially prepared wood chips in digesters of 80 to 200 cc. capacity under closely controlled conditions in regard to time, temperature, alkali concentration and pressure. The experimental conditions could then be varied one at a time and the resulting pulp examined for yield and carbohydrate, lignin content and quality, in accordance with a standardized procedure.

This technique has been described in detail by Macklin and Maass (3) and is briefly as follows: In those experiments requiring a continuous flow of liquor of constant composition through the digester during the cooking process, an Allegheny metal cell of 80 cc. capacity was charged with 10 gm. of air-dry wood chips 2 by 10 by 20 mm. The cell was thoroughly evacuated at a pressure of about 2 cm. of mercury. The cooking liquor was then introduced under a pressure of 125 lb. per sq. in. (gauge). It flowed through the cell at the rate of 5 cc. per min. during the entire period of digestion. In this manner, the liquor concentration in the cell remained constant during the delignification reaction. The cell was heated and electrically controlled at 160° C. in an oil bath. The wood used was naturally seasoned black spruce, the chips being cut along the grain. Their density and original lignin content is indicated in each set of experimental results. This procedure is called "forced penetration" of the liquor, with pre-evacuation and liquor flow. An alternative procedure was "natural penetration" of the liquor, in which the liquor was added to the chips at atmospheric pressure and without any pre-evacuation of the wood. The pressure within the chip then built up slowly as the temperature was raised, and penetration of the cooking reagent into the wood was hindered by the presence of the air in the wood.

At the end of the digestion period, which was usually of three hours duration, the reaction was stopped by plunging the cell into cold water.

The cooked chips were broken up into single fibres by a motor-driven, propeller type of disintegrator, and thoroughly washed. Approximately 1.2 gm. (air-dry basis) of the wet pulp was made into a hand sheet. After it had been conditioned for two hours at 65% relative humidity and 70° F., the sheet was tested for bursting strength on a motor-driven Mullen tester, according to the standard procedure set by the Technical Section of the British Paper Makers Association (5). The bursting values obtained were converted into per cent Mullen on the basis of 25 by 40 in. 500 sheet ream by multiplying the mean burst value observed by the factor 2.82 and dividing by the air-dry weight (in grams) of the sheet.

The remainder of the pulp, and the test sheet were then dried to constant weight in an oven at 105° C., and the yield of pulp was expressed as a percentage of the original bone-dry wood. Half-gram samples of the pulp were then analyzed for lignin content by the formaldehyde-sulphuric acid method, as described by Macklin and Maass (3). The lignin is expressed as a percentage of the original bone-dry wood.

Experimental Results and Discussion

A number of experimental conditions that might be capable of influencing the penetration of the alkaline pulping liquor into the wood chip have been investigated separately. Since these conditions are largely unrelated to one another, except in so far as they may simultaneously affect the process, it was considered advisable to present and discuss these factors under a number of separate headings. In each set of experimental results, the procedure used was that described above, unless otherwise modified as indicated. Detailed observations have been omitted, and the results have been tabulated to an extent considered compatible with clarity. A short discussion follows each set of experimental results.

Previous investigators of the soda process have used wood chips that were only approximately uniform in size in order to obtain comparable and reproducible results. In the present investigation however, one standard size of chip, 20 by 10 by 2 mm. was used throughout in order to compare the influence of different variable factors under similar experimental conditions. Nevertheless, it was deemed important to determine at the beginning of the investigation the limiting size of chip at which diffusion processes began to seriously hinder the rate of delignification, and second, whether the rate of delignification of very fine wood-meal was higher than that of chips of standard size.

Wood-meal

In this series of experiments, wood-meal of 250-300 mesh screen, which had been extracted with water, alcohol-benzene and methyl alcohol, was used. It therefore contained only cellulose, lignin and hemicellulose. The digestion was carried out with natural penetration of the liquor, in cast-iron bombs of 200 cc. capacity containing 165 cc. of 2.0 *M* sodium hydroxide at 160° C. The lignin contents of the resulting pulps and the values obtained with chips of standard size are reported in Table I.

TABLE I
DELIGNIFICATION OF WOOD-MEAL

Time, hr.		0.0	1.08	1.75	3.0
Lignin in pulp, %	Wood-meal	30.1	21.0	15.2	7.8
	Wood chips	30.2	21.5	14.6	7.6

The results were confirmed with wood-meal and chips prepared from a sample of a different density. In every case, identical residual lignin values were obtained in the pulp whether the wood used was in a finely comminuted state or chips 20 by 10 by 2 mm.

It is surprising that the extent of the delignification at different time intervals during the process should be no greater with a finely ground 250–300 mesh material (particle size of about 0.005 mm. in diameter) than for chips 2 mm. in thickness. This indicates, primarily, that the diffusion of the alkali into, and of the reaction products through, the cellular passages of a chip of this size is not a factor that affects the rate of reaction; and secondly, that the lignin present in a finely ground wood-meal having a particle size of 0.005 mm. does not dissolve more readily than the lignin that is embedded in the cellulose in the solid wood chip. All the lignin is equally accessible to the reagent, and therefore there is in effect a homogeneous type of chemical reaction.

The Influence of Chip Size

The next step was to determine the maximum chip size, above which the wood structure hindered the penetration of the alkali and the outward diffusion of the reaction products sufficiently to affect the rate of delignification. Since Lusby and Maass (2) had shown that diffusion of sodium hydroxide in aqueous solution took place with equal rapidity in the three structural directions of wood chips, it was decided to use cubical wood specimens of 10, 15 and 20 mm. edge, in this part of the investigation.

Two different experimental procedures were used. In the first, termed "forced penetration", the chips in the cell were evacuated, and liquor was then introduced under 125 lb. pressure (gauge). The wood was impregnated with liquor at the very start of the cook, so that penetration of the alkali could then take place freely, by processes of diffusion and unhindered by the presence of air.

In the second procedure, called "natural penetration", there was neither evacuation nor application of pressure. The chips were simply covered with liquor in a cast-iron bomb. With rise in temperature, penetration took place slowly under the vapor pressure of liquid, and retarded by the presence of the air phase in the chip.

With these two different methods of procedure, cooks were carried out with black spruce wood of density 0.43 and lignin content 30.9%, at 160° C. for various lengths of time with 2.0 *M* sodium hydroxide. The residual lignin content of the pulped chips is given in Table II.

In the case of the three pulp samples marked with an asterisk, a considerable portion of the yield, namely 10% of the 15 mm. chips and 29 and 42% of the 20 mm. chips consisted of hard uncooked wood with a lignin content of 30 to 36%. On the other hand, no hard uncooked centres were observed in the chips that had been cooked with forced penetration of the liquor, although of course shives were present till the third hour.

TABLE II
CHIP SIZE AND DELIGNIFICATION

Time, hr.	Dimensions of chips, mm.				
	2 by 10 by 20	10 by 10 by 10	15 by 15 by 15	20 by 20 by 20	
	Lignin in pulp, %				
<i>"Forced" liquor penetration</i>					
0.00	30.9	30.9	30.9		Only shives Few shives Well cooked
1.00	21.0	22.8	27.0		
2.00	12.5	12.5	17.5		
3.00	7.8	8.5	11.5		
<i>"Natural" liquor penetration</i>					
0.00	30.9	30.9	30.9	30.9	
1.75	—	—	—	20.1*	
3.00	6.3	8.7	11.1*	12.2*	

This gives some indication of the extent to which the presence of air can retard the cooking process by interfering with the entry of the cooking liquor into the interior of the chip.

In both procedures the chips kept their shape throughout the cook, and the progress of the cooking action could be followed by cutting the chip in half and examining it in cross section. Cooking was observed to take place in three separate stages from the exterior of the chip inwards, and could easily be followed by the color changes taking place.

In the first stage, following the penetration of the liquor, there was a slight softening of the chip, and the wood was still light in color. Some of the pentosan material having been dissolved, the lignin content accordingly rose above that normally present in wood. Such a chip would not be mechanically disintegrated into pulp fibres. This condition still prevailed in the interior of the 15 mm. and 20 mm. chips that had been cooked for three hours without pre-evacuation or forced liquor penetration, but was absent in the other chips.

In the second stage, the outer portions of the chip became softer and darker. The distinct boundary line separating this softer portion from the hard yellow centre moved slowly inwards until the chip was uniform in appearance and texture throughout. The chip could then be completely disintegrated into pulp and fine shives, but could not be entirely broken up into individual fibres. This pulp made a fairly good sheet having a strength value of from 60 to 80 M.B.R. The yield would be 55% or more, and the lignin content about 18% on a pulp basis.

In the third stage of the pulping process, the chip became much softer and lighter in color. This corresponded to the removal of the remaining lignin from the middle lamellae, and the chips could be completely disintegrated into individual fibres. At this stage, pulp yields fell below 50%, and a point

is reached where, in commercial operation, the decrease in lignin content no longer compensates for the simultaneous loss of cellulose, and it is more profitable to stop the digestion at this stage and remove the remaining lignin by a bleaching operation.

In conclusion, it may be stated that the rate of delignification is the same irrespective of the size of the chip, from 250 mesh particles up to cubical chips of 10 mm. edge. For chips of greater thickness than 10 mm. but less than 20 mm., the reaction is greatly retarded by the resistance to penetration offered by the air-phase in the chip. In the absence of this air, the rate remains substantially unaffected. For chips that are 20 mm. and more in thickness, diffusion processes begin to retard the reaction rate even when the air in the chips has been removed.

The slower delignification rate observed with the chips of larger size may be attributed to two causes. Either the alkali is being used up more rapidly in the interior of the chip than it can be supplied by diffusion, or else the outward diffusion of the reaction products may have been retarded sufficiently to accumulate in the interior of the chip, and interfere at the reaction interface. Either phenomenon would cause the observed decrease in reaction rate, and will be discussed in greater detail in a subsequent paper dealing with the mechanism of the reaction.

For the present, the effect of penetration in subsequent work will be eliminated by the use of a standard wood chip 2 mm. thick, 10 mm. wide and 20 mm. long in the fibre direction.

Wood Density

The spruce wood used in commercial pulping practice is found to vary considerably in density. The average sample has a bone-dry specific gravity of about 0.45, but wood specimens of density 0.35 or 0.55 are quite common. Such variations in the density of the wood structure might be expected to affect the liquor penetration. Furthermore, a higher lignin content is generally associated with the denser wood. It was interesting therefore to determine how the high density wood differed from the low density wood in behavior on delignification. Three different experimental procedures were used, in order that the conclusions might be general in their application.

In Series I, a cell of 80 cc. capacity was used with 10.0 gm. of 20 by 10 by 4 mm. chips, with pre-evacuation and forced penetration of the liquor, but without liquor flow during the course of the digestion. In Series II, the conditions were the same except that fresh liquor flowed continuously through the cooking cell during the reaction. In the third series, bombs of 200 cc. capacity were used, with natural penetration of the liquor. The wood in every case was cooked for three hours at 160° C. in accordance with the standard procedure.

The resulting yields of lignin and carbohydrate, expressed as a percentage of the original bone-dry wood are given in Table III, together with the density of the wood and the strength of the resulting pulp.

It is to be noticed that: (i) The wood of higher density gave a pulp of higher lignin content, but only to the extent which would be expected from the higher lignin content originally associated with the wood of higher density. (ii) Higher yields of carbohydrate were always obtained from the woods of lower density, in accordance with their lower lignin contents. (iii) There is a marked decrease in paper strength with increase in wood density, which is to be ascribed to the shorter fibre length of the high density wood. (iv) These conclusions were found to hold, independently of the particular cooking procedure followed.

TABLE III
THE EFFECT OF WOOD DENSITY

Series	Wood density	Lignin, %	Carbo-hydrate, %	Strength, % Mullen
I	0.34	3.8	45.1	114
	0.54	5.6	42.6	80
II	0.41	3.7	42.4	144
	0.51	4.6	39.8	116
III	0.35	2.8	41.0	113
	0.45	3.4	40.5	97

Moisture Content

In commercial wood-pulping practice, wide variations occur in the moisture content of the wood. The wood may have been stream-driven and contain 40% of water, or it may have been kept in storage for one or more years, and have a moisture content as low as 6%. This is a variable that might influence the reaction, since the imbibition of moisture is accompanied by a swelling of the wood and a constriction of the passages available for liquor penetration. It was therefore desirable to determine what effect the initial water content of the wood had upon the cooking results.

The standard size of chip, 20 by 10 by 2 mm. was used, with 2.0 *M* sodium hydroxide liquor, and cooked for three hours at 160° C. In the first set of experiments, a bomb of 80 cc. capacity was employed containing 10 gm. of wood and 18 gm. of water. No correction was made to the liquor concentration for the dilution caused by the water

TABLE IV
EFFECT OF MOISTURE CONTENT UPON DELIGNIFICATION

Series	Moisture, %	Lignin, %	Carbo-hydrate, %	Strength, % Mullen
I	6.6	6.8	47.0	110
	180.0	3.3	45.3	113
II	6.8	4.5	44.3	107
	86.0	3.9	43.6	to
	100.0	3.6	46.9	
	180.0	3.9	44.8	111

content of the chips. In the second set, bombs of 200 cc. capacity were used containing 165 cc. of 2.0 *M* liquor, the liquor concentration being corrected for the decrease in concentration caused by the water present in the chips.

It is seen that if the liquor is corrected for the decrease in concentration brought about by the water content of the chips, then the presence of moisture has no effect upon either the extent of delignification or the strength of the pulp. This holds only for alkali cooking; deMontigny (1) has shown that in sulphite cooking an increase in moisture content from 18 to 84% brings about an increase in lignin content from 4 to 15% and a decrease in paper strength from 260 to 125% Mullen. The reason for this difference in behavior is that, in sulphite cooking, the liquor has not as great an initial solvent action upon the incrusting materials as has the sodium hydroxide liquor. Consequently, liquor penetration has to take place almost entirely from tracheid to tracheid along the fibre direction of the wood, in which case, as Sutherland (4) has shown, the forced penetration is hindered by a "Jamin tube" effect. Drops of liquid and bubbles of gas alternate in the tracheid of wood of a high moisture content. As a result, such a system transmits less pressure than it receives. The forced penetration of the sulphite liquor into the chip is therefore retarded, and pulps of high lignin content and low strength are obtained.

On the other hand, Lusby (2) has shown that, in soda cooking, penetration takes place with equal ease in the three structural directions of the wood, owing to solvent action in the initial stages of the penetration process. Consequently, the presence of moisture up to saturation presents no difficulty to liquor penetration by diffusion. The only noticeable effect is the dilution of the liquor resulting from the higher water-content of the wood.

The observed variations in carbohydrate yield may be due to errors inherent in the method, because with such a heterogeneous substance as wood the yield values are subject to erratic and inexplicable variations, so that only the mean value obtained from several experiments carried out under identical conditions can be taken as an indication of how the yield was influenced by a certain treatment.

Wetting Agents to Assist Penetration

It has been previously shown that, for chips below a certain size, resistance to penetration is not sufficient to influence the rate of the delignification reaction. However, it might be that in all these cases a slower submicroscopic penetration of the alkali ions into the fine gel structure of the wood and lignin is taking place. This submicroscopic penetration might be the factor limiting the reaction rate. It was thought, therefore, that if traces of the sulphonated fatty alcohols were added to the cooking liquor, they would lower the surface tension of the advancing liquor phase and might cause a more rapid and thorough impregnation of the ultimate wood substance, and thus favorably influence the properties of the pulp. A number of such wetting agents, of the general formula $R \cdot OSO_3 \cdot Na$ were therefore added in small amounts to the cooking liquor. Compounds *A* and *B* are the sodium salts of the sulphonated lauryl and oleyl alcohols. *C* is a similar compound but of higher molecular weight. *D* is a sulphonated naphthalene derivative.

The wetting agents were added to the extent of 0.2% to 165 cc. of 2 *M* sodium hydroxide liquor and 10 gm. of wood chips of the standard size. The chips were cooked at 160° C. for three hours, and without any preliminary forced penetration of the liquor into the chips. In Table V is given the percentage yield of pulp and the bursting strength of the paper made therefrom which is a good measure of the pulp quality.

TABLE V
THE INFLUENCE OF WETTING AGENTS ON PENETRATION

Wetting agent	None	A	B	C	D	D (0.04%)
Pulp yield, %	44.2	43.7	43.7	41.7	43.3	43.2
Pulp strength, % Mullen	115	88	106	92	108	108

The effects observed were small, however, and generally unfavorable. It would seem therefore that sulphonated fatty alcohols added to the alkali liquor in small amounts do not markedly affect the results of the soda process by facilitating the liquor penetration. The effect upon paper strength is small and generally unfavorable.

Conclusions

The salient facts that arise from a consideration of the influence of liquor penetration in the alkaline delignification of wood are the following: In general, the wood structure offers but little hindrance to the delignification reaction for chips up to 10 mm. in thickness, even with completely air-filled wood. A very finely ground wood-meal gave no increased rate of reaction. Moreover, the presence of moisture in the wood to the extent of fibre saturation was without pronounced influence upon the reaction rate, and the delignification was not sensibly different in wood specimens of high density. No advantage furthermore was to be gained through the addition of wetting agents to the cooking liquor in order to facilitate the penetration process.

In general, therefore, it can be stated that penetration of the soda liquor into the gross structure of the wood substance, and the outward diffusion of the reaction products, are not the determining factors in fixing the velocity of the rate of delignification.

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EQUILIBRIA IN LIQUID SYSTEMS CONTAINING FURFURAL¹By B. A. LLOYD², S. O. THOMPSON³ AND J. B. FERGUSON⁴

Abstract

The solubility curves and tie-lines at 25° C. were determined for the systems acetone-water-furfural, water-furfural-ethyl acetate and water-furfural-isoamyl acetate.

Introduction

The mutual solubilities of water and furfural were studied by Rothmund (13), Mains (9), and Evans and Aylesworth (3). Qualitative information concerning more complicated systems containing furfural has been given by Jänecke (8) and especially by Hammer (5). There is little, if any, quantitative information on such systems in the literature. An extended study of the more common solvents is not to be expected, but a limited amount of quantitative information on each solvent should be available.

Materials and Procedure

The furfural was purified by steam and by vacuum distillation. It boiled at 161.7° C. \pm 0.1°. It was kept in dark colored bottles (9, 12) and no material was used that was more than a week old (4). The purity of the furfural was checked by the redetermination of the solubilities for the system water-furfural, using the procedure of Mueller (11). The results so obtained agreed with those of Evans and Aylesworth. A badly discolored sample was used to test the effect of the impurities on the solubility. The saturated solutions were not particularly sensitive to these impurities; for example, the consolute temperature was raised from 118 to 120° C. in one experiment.

C.p. acetone was dried and redistilled; c.p. isoamyl acetate was fractioned by distillation and the fraction that was taken boiled at 141.6° C. \pm 0.1° at 754 mm. of mercury. C.p. ethyl acetate was washed with water and distilled. The fraction that was used had a density $D_4^{20} = 0.9006$; Wade and Merriman's value (14) was $D_4^{20} = 0.90056$.

The solubility curves at 25° C. were determined by titration. The container was a Pyrex glass tube, 12 mm. bore and 60 mm. long, sealed at both ends. A tube of 3 mm. bore, through which the reagents were introduced, was sealed to the side of the Pyrex tube. A known two-component sample was placed in the container and the latter was put in a thermostat, kept constant at 25° C. \pm 0.1°, so that the side tube projected above the bath liquid. The third component was introduced by means of a small weight burette equipped with a long fine delivery tip. The side tube was stoppered when not in use. Stirring was effected by a suitable rotation of the container in a plane that differed slightly from the horizontal. This caused the gas bubble, present in the large tube, to move from one end of it to the other and thus to stir the liquid.

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The tie-lines were obtained from the weights of the two phases in a sample of known composition by the method of Miller and McPherson (10), or from these weights and the furfural content of the furfural-rich phase. Furfural was determined by the colorimetric method of Fleury and Poriot (15, p. 419). The known sample was placed in a glass vessel somewhat similar to an Ostwald pycnometer, but with longer capillary leads that projected above the bath liquid. After shaking, the phases were allowed to separate at constant temperature. The lower phase was removed through the lower capillary without exposing the main part of the container to the air. The weights of the separated phases were checked against the total weight of the sample.

The plait point for the system acetone-water-furfural was approached experimentally, and checked by the extrapolation of the line through the mid-points of the tie-lines.

Results

The binary solubilities for furfural-water had not been determined at 25° C. For water in furfural the value that was obtained by the interpolation of the results of Mains was satisfactory, but the corresponding value for furfural in water did not agree with the writers' results for the ternary systems, and Thompson's value was substituted for it. The mutual solubilities of water and isoamyl acetate were so small that Bancroft's value (1) at 20° C. was assumed to be satisfactory for 25° C. The mutual solubilities of ethyl acetate and water are given in I.C.T. (7, p. 388), and these were confirmed by the writers.

The binodal curve, the tie-lines and the plait point for the system acetone-water-furfural are shown graphically in Fig. 1. Owing to the large areas of

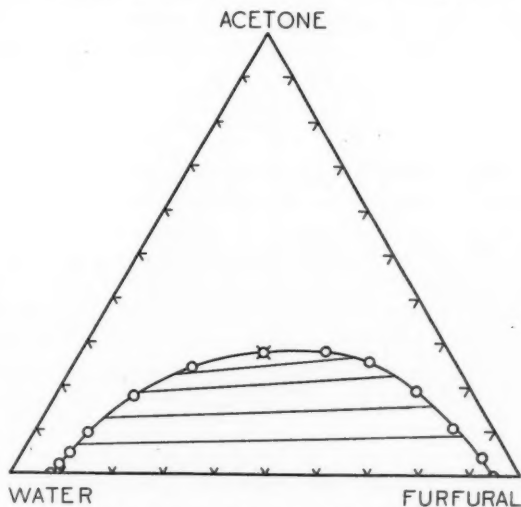


FIG. 1. The binodal curve, the tie lines and the plait point for the system acetone-water-furfural at 25° C.

immiscibility on the phase diagrams for the other systems, these diagrams are not given. The numerical results are listed in Tables I, II and III.

TABLE I
THE SYSTEM ACETONE-WATER-FURFURAL AT 25° C.
Weight percentage— $a + b + c = 100$

The binodal curve			
Acetone (a)	Furfural (c)	Acetone (a)	Furfural (c)
0.0	7.7	0.0	94.7
2.2	8.5	4.0	90.3
4.7	9.3	10.6	81.6
9.4	10.5	19.3	70.1
17.9	15.1	25.8	57.7
24.1	23.4	28.0	47.8
	Plait point	27.4	35.8

The tie-lines				
	The furfural content			
Phase I	21.0	16.0	12.2	10.0
Phase II	53.5	64.0	74.5	84.0

TABLE II
THE SYSTEM WATER-FURFURAL-ISOAMYL ACETATE AT 25° C.
Weight percentage— $a + b + c = 100$

The water-rich phase		The water-poor phase	
Furfural (<i>b</i>)	Isoamyl acetate (<i>c</i>)	Furfural (<i>b</i>)	Water (<i>a</i>)
0.0	0.2	0.0	1.2
1.8	0.5	9.7	1.1
3.8	0.4	19.7	1.6
5.8	1.2	29.5	1.8
7.3	1.9	39.9	2.1
7.7	0.0	43.2	2.2
		48.2	2.4
		53.5	2.9
		58.4	2.6
		78.4	3.6
		88.8	4.6
		94.7	5.3

The tie-lines

The furfural content	Phase I		Phase II	
	2.0	16.0	4.2	36.0

TABLE III
THE SYSTEM WATER-FURFURAL-ETHYL ACETATE AT 25° C.
Weight percentage— $a + b + c = 100$

The water-rich phase		The water-poor phase	
Furfural (<i>b</i>)	Ethyl acetate (<i>c</i>)	Furfural (<i>b</i>)	Water (<i>a</i>)
0.0	7.56	0.0	3.24
1.7	6.6	3.3	3.5
3.9	4.9	6.9	3.4
5.3	3.2	15.8	4.3
6.5	2.4	21.9	4.2
6.8	1.9	33.3	4.1
7.4	0.6	51.4	4.4
7.7	0.0	60.7	4.8
		71.9	4.6
		74.7	4.9
		86.3	5.1
		94.7	5.3

The tie-lines			
	The furfural content		
Phase I	3.8	5.0	6.7
Phase II	31.9	70.5	90.1

Discussion

In the system water-acetone the partial pressures at 25° C. (2) show a large positive deviation from Raoult's law, and one might infer that the system is not far removed from systems that show liquid immiscibility. For this reason, a greater area of immiscibility was expected than is shown in Fig. 1. The tie-lines for this system do not agree closely with the empirical equation of Hand (6),

$$\frac{a}{b + kc} = \frac{a'}{b' + kc'}$$

but there can be no doubt that this equation offers a practical solution of the problem of the interpolation between determined tie-lines for many cases of dineric distribution.

The water-rich and the water-poor series of saturated solutions in the systems that contain ethyl acetate or isoamyl acetate should each lie on curves that intersect. When the results given in Tables II and III are plotted, definite breaks are evident for the water-rich series. There is an indication of a break on the water-poor isoamyl acetate curve at 45% of this component, but there is none on the corresponding ethyl acetate curve, although the tie-lines indicate there should be one at approximately 90% furfural. Since the solutions of furfural in ethyl acetate and in isoamyl acetate do not dissolve more water than do the pure solvents, these solutions would not be expected to dissolve water-soluble materials to a much greater degree, and in this respect should be as efficient differential solvents.

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THE BASE-EXCHANGING PROPERTIES OF SYNTHETIC ALUMINO-SILICATE MATERIALS. II.¹

BY J. R. PATTON² AND J. B. FERGUSON³

Abstract

The base-exchanges $\text{Ca}^{++} \rightleftharpoons \text{Na}^+$ and $\text{Ba}^{++} \rightleftharpoons \text{Na}^+$ have been studied with Doucil and various salt solutions. The calcium or barium content of the gel increased as the concentration of the solution decreased. With the more concentrated solutions, the calcium content of the gel increased with increasing temperature; at the same temperature, the calcium content was greater when calcium Doucil replaced sodium Doucil as the initial gel material. Solutions of calcium nitrate and of calcium acetate gave similar results, but these were higher than those obtained with calcium chloride solutions.

The exchange reaction is chiefly determined by the relative cationic content of the gel and of the solution, but the actual amount of exchange taking place in a given case is greatly dependent upon the available capacity, which is in turn dependent upon those factors that affect the penetration of the gel. The effects of temperature, of concentration, of the kind of anion and of the kind of gel are thought to be more closely related to the penetration phenomena than to the exchange reaction proper. Although the direction of the effect of concentration is indicated by the equation of Rothmund and Kornfeld, the results are not in quantitative agreement with this equation. The equation $\frac{P}{E_1} = a + bP$ is useful for the interpolation of curves obtained at constant anionic normality, especially if the solutions are dilute.

Introduction

The base-exchange reaction with artificial alumino-silicate gels usually proceeds rapidly at first, and then so slowly that a state of equilibrium is commonly assumed to have been reached at this stage. The steady states probably represent a close approximation to states of equilibrium involving those portions of the solid in which a rapid diffusion is possible. This diffusion is dependent upon various factors, and it is not easy to determine the amount of the solid that is reacting, or, in other words, the actual capacity. Many of the published base-exchange curves are a record of the above-mentioned steady states, and their actual significance needs further elucidation.

The earlier paper (1) dealt with the base-exchanges $\text{Ag}^+ \rightleftharpoons \text{Na}^+$ and $\text{Cu}^{++} \rightleftharpoons \text{Na}^+$. The work has now been extended to include the reactions $\text{Ca}^{++} \rightleftharpoons \text{Na}^+$ and $\text{Ba}^{++} \rightleftharpoons \text{Na}^+$ with Doucil as the gel material.

Experimental

The Doucil was selected from a large sample of commercial material. The analysis by Patton is: Na_2O , 10.29; Al_2O_3 , 14.86; SiO_2 , 53.08%. Water was not determined. The corresponding weight percentages given by Musgrave for his Doucil were: 10.26; 14.65 and 52.35.

The samples of gel material were ground to pass a 100 mesh screen and the portions that were retained on a 200 mesh screen were used. A weighed amount of this material was placed in a glass-stoppered bottle to which was

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added a known amount of a known salt solution. The selection of the proper amounts was simplified by the use of the linear relation employed in Fig. 2 when the approximate position of the curve was known. The bottle was placed in a thermostat and shaken for 1.5 hr. Trial experiments showed that a steady state was reached within an hour, and that this state was not appreciably changed at the end of 12 hr. if calcium nitrate solutions were used. The bottle was removed from the bath and the contents filtered and analyzed. Since the amount and the composition of the gel and of the solution initially taken were known, the amount of one base in the final solution sufficed for the calculation of the composition of the final solution and of the amount of the exchanged base in one unit of the final gel. The change in the composition of the solution was assumed to be caused by an exchange reaction with the gel.

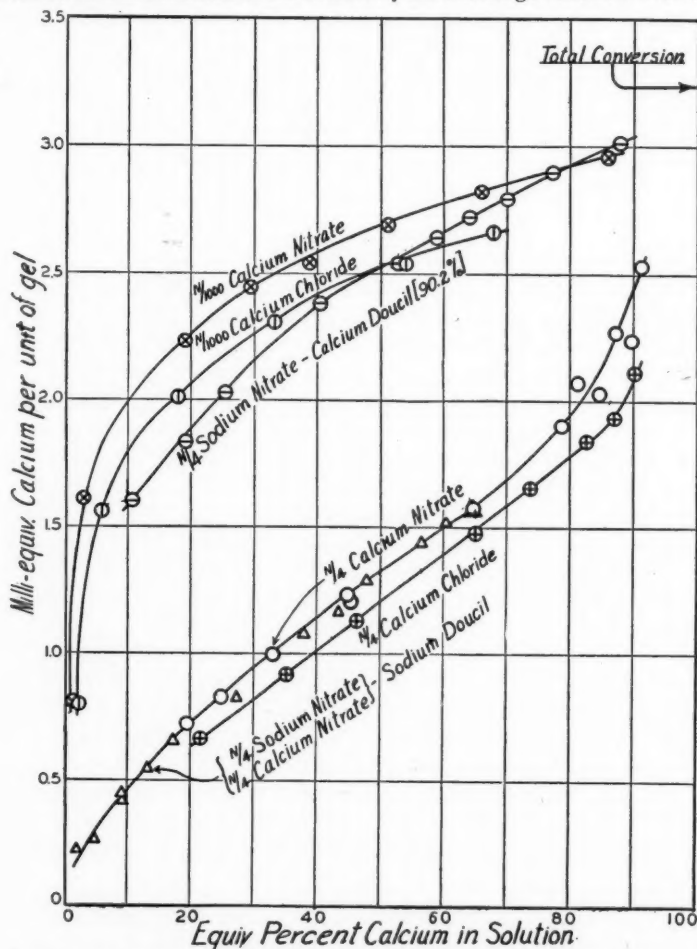


FIG. 1. The Doucil base-exchange curves for the $\text{Ca}^{++} \rightleftharpoons \text{Na}^{+}$ reaction at 21°C .

Calcium was determined as the oxalate, and barium as the sulphate. Sodium Doucil was decomposed with aqua regia. Calcium Doucil was fused in a nickel bomb with sucrose and sodium peroxide. When decomposed, the gels were analyzed by the standard methods for rock analysis. The very dilute solutions were concentrated on a water bath, and blank determinations were made in all cases. In the experiments with $N/1000$ solutions, the blanks consisted of duplicate experiments in which distilled water was substituted for the salt solutions.

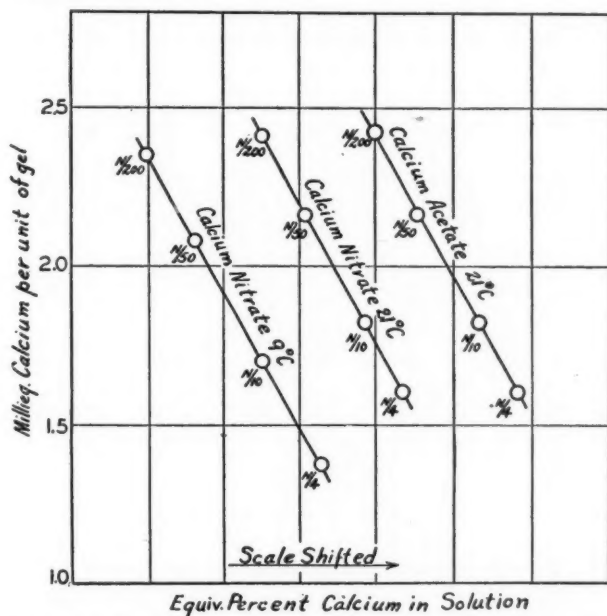


FIG. 2. The effects of temperature and of anionic concentration upon the $\text{Ca}^{++} \rightleftharpoons \text{Na}^{+}$ reaction. (Initial ratio, calcium in solution : sodium in gel = 1.2 : 1).

A pure calcium Doucil could not be prepared directly from sodium Doucil. Successive treatments with $N/2$ calcium nitrate solutions extending over 24 hr. gave a conversion of 69.7%, and a similar treatment with $N/1000$ solutions gave 80.7%. This value was raised to 90.2% when the treatments were continued for several weeks.

The ratio of the calcium in the initial solution to the sodium in the initial gel was kept constant at 1.2 : 1 in the experimental series that illustrate the effects of temperature and dilution. Under these conditions the points that were obtained for each series would lie on a straight line when plotted on a diagram similar to that given in Fig. 1. Similar lines are shown in Fig. 4 of the earlier paper.

The calcium-sodium curve at $N/4$ was obtained with pure calcium nitrate solutions and also with solutions of calcium and sodium nitrates. In the

latter, the ratios of the bases (sodium to calcium) varied from 0.1 to 50, and the weights of Doucil for the two series varied from 0.2 to 15 gm. Although the initial conditions were so different in these experiments a concordant set of results was obtained, and hence the solution volume was not important at constant anionic normality. However the $N/4$ calcium chloride curve and the various curves at $N/1000$ were obtained at constant volume for each curve. The three upper points on the calcium Doucil curve at $N/4$ were obtained with mixed solutions of different volumes, and the other points were obtained with sodium nitrate solutions and at constant volume. There is no break in the curve to indicate the change in the experimental conditions.

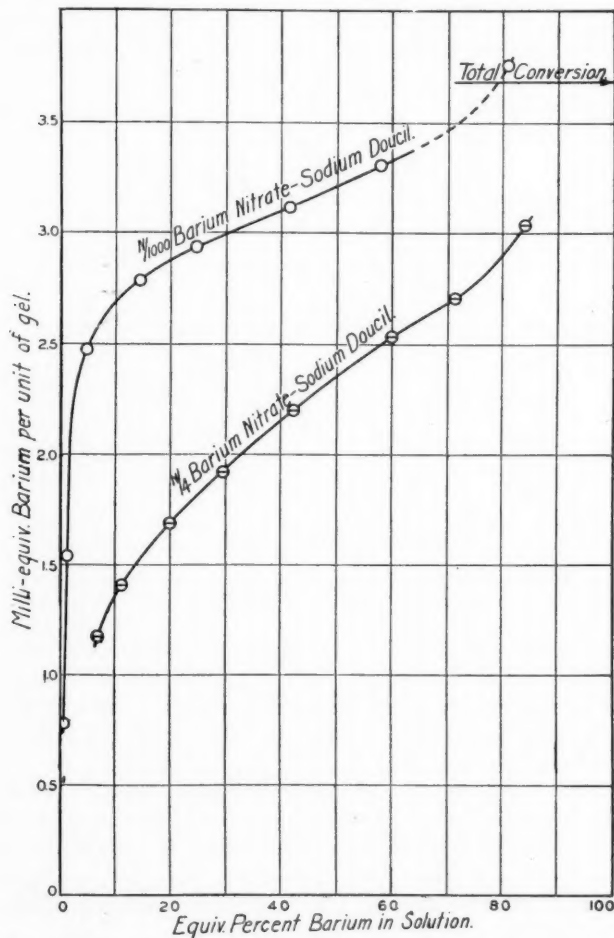


FIG. 3. The Doucil base-exchange curves for the $Ba^{++} \rightleftharpoons Na^{+}$ reaction at $21^{\circ} C$.

In the presentation of the results, the base content and not the true cationic content is used; the former is considered as though it were identical with the latter. In Figs. 1, 2 and 3, the writers have plotted E'_1 , the milli-equivalents of the entering cation in the final gel, against P , the equivalent percentage

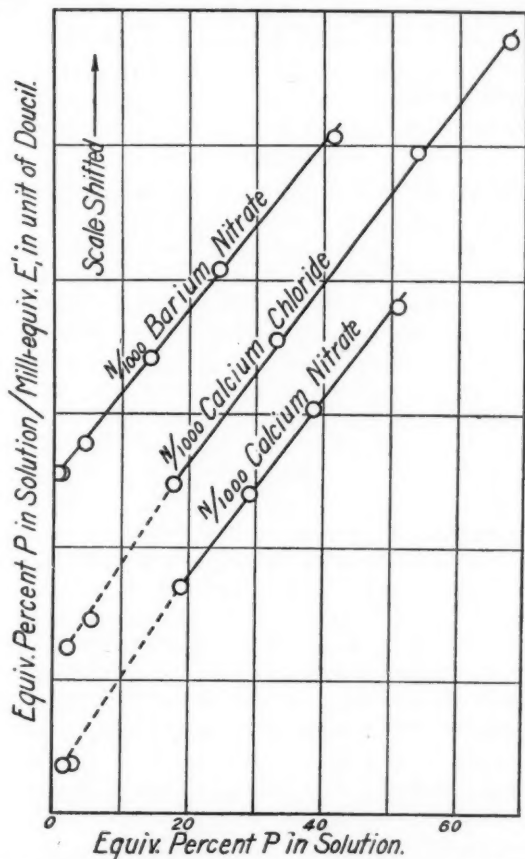


FIG. 4. The barium and calcium base-exchange results at great dilution. (To illustrate the use of the equation $\frac{P}{E'_1} = a + bP$.)

(bases only) of this cation in the final solution. P may be defined as $\frac{E_1}{E_1 + E_2} \times 100$. The corresponding percentage $\frac{E'_1}{E'_1 + E'_2} \times 100$ for the gel is not a suitable variable because the gel capacity ($E'_1 + E'_2$) is uncertain. At constant gel capacity, E'_1 is proportional to this percentage, and the use of it does not materially affect the shapes of the curves. In this way the functional relation that exists between the relative cationic content of the

final gel and of the final solution may be indicated, although the actual gel capacity may be unknown. The gel unit contained initially 3.68 milli-equivalents of sodium.

The calcium-sodium results are indicated in Fig. 1, and the barium-sodium results in Fig. 3. The temperature and dilution series for calcium-sodium are given in Fig. 2. Had the scale not been shifted, the lines would all pass through the point 100 on the abscissa. Fig. 4 shows the range of solution compositions over which the equation $P/E'_1 = a + bP$ is applicable at high dilution.

Discussion

The capacity of a gel for a particular base-exchange reaction must be obtained either from some direct measurement or from the exchange curve. Neither of these methods can be used with assurance. The curves are usually smooth over a wide range of P -values, but in many cases they turn up at their upper ends. There is no accepted method for the extrapolation of the central smooth portion, and the capacity that is obtained from experiments with successive treatments with the pure salt solutions may not be the proper capacity for this smooth part of the curve.

As the concentration of the solution decreases from $N/4$ to $N/1000$, the curves gradually change in shape and become similar to the curve for the $\text{Ag}^+ \rightleftharpoons \text{Na}^+$ reaction. This was evident in the uni-divalent exchanges with copper, with calcium, and with barium. Since the $\text{Ag}^+ \rightleftharpoons \text{Na}^+$ reaction was apparently independent of the concentration of the solution at such normalities, this trend is significant. The curves at the low concentrations are evidently a better measure of the true exchange reaction than are those for the higher concentrations. Some might regard the curves at $N/1000$ of dubious value, but they are supported by the results at the intermediate concentrations. If one extrapolates upward the $N/1000$ calcium nitrate curve, it cuts the axis at a point close to 3.03 milli-equivalents. The calcium content of the 80.7% calcium Doucil was 2.97 milli-equivalents. Since the former value was obtained from experiments of one and one-half hours' duration and the latter from an experiment lasting 24 hr., it is but reasonable to assume that the capacity for this curve is close to these values. It may be noted that a maximum conversion of 90.2% or 3.32 milli-equivalents was obtained in prolonged experiments and that the initial base content of the gel was 3.68 milli-equivalents. Neither of these values appears suitable, and the question of the capacity is apparently one that must be considered separately for each case. A similar treatment cannot be given the $N/4$ curves, since they do not appear to be single curves. The proper capacity cannot be determined for any portion of them. Extrapolation is a doubtful procedure, and the tendency of the curves to rise at their upper ends makes the capacity that is found by successive treatments with pure salt solutions of doubtful significance.

Many experiments suggest that the position of the exchange curve may be a rough gauge of the capacity. The relative positions of the curves are in

qualitative agreement with the conversions that are obtained with successive amounts of the pure salt solutions. Dilute solutions are better than strong ones, and copper enters the gel more readily than calcium. In one experiment, sodium Doucil was treated with successive amounts of $N/2$ cupric nitrate solution for 24 hr. (total), and this yielded a conversion to copper Doucil of 85.4%. This conversion was not increased by subsequent treatments with any other solution that was tried, including the $N/1000$. But the latter solution, when used initially, produced a 98% conversion in 24 hr. The calcium nitrate solutions under similar conditions gave conversions of 69.7 and 80.7% respectively.

If the position of the exchange curve be taken as an indication of the actual capacity, it follows that comparisons of the exchanging power of various cations are often comparisons of capacities. This is particularly true in those cases in which the curves flatten at high solution percentages, and the points selected for comparison are in this region. Renold's (2) comparisons are often of this type. Many have used the amount of added salt for one variable, instead of the equivalent percentage for the solution, which is used in this paper. Points are selected for comparison that correspond to the same amount of added salt, usually an amount equivalent to the base content of the gel. This method may be illustrated by Fig. 1. It is a comparison of the point on the upper curve at $P = 33.6$ with the point on the lower curve at $P = 62$. In general, one would expect this comparison to be more a function of the shape of the exchange curve in addition to the capacity than would be a comparison at a high value of P such as 70. This may be an advantage for some purposes, but this method of representing exchange results is open to the criticism that the important variables, the cationic content of the solution and of the gel are not both used, and the former is a function of the two variables that are used. Moreover the use of diagrams that are of the infinite type avoids the questions raised by the finite diagram, and hence minimizes the importance of the upper parts of the exchange curves and of the actual capacity.

Renold has concluded that many of his results with Permutite are best explained by the assumption that a certain blocking of the diffusion paths takes place in the gel. The writers believe that the available capacity for a given reaction is greatly affected by the ease with which the entering cation can enter the gel. The observations of the writers and of others seem to show that the ability to penetrate a gel is a specific property of the cation or cationic complex. The blockage of the diffusion paths also seems important, and no doubt plays an important part in the influence of temperature and of anionic concentration on the reaction, as indicated by the writers' various uni-divalent results. These matters are of utmost importance to those interested in the actual amount of exchange that takes place, but the available capacity and the exchange are different entities. The rules that govern these may have some qualitative similarities, but it is most unlikely that the rules are in any case identical. For example, the cationic hydration may be

an important factor in the penetration and in the exchange reaction, but a correlation between the extent of the hydration and the total amount of exchange does not necessarily yield accurate information about the exchange process at constant capacity.

The separate curves for the silver nitrate-sodium Doucil and for the sodium nitrate-silver Doucil reactions that were given in the first paper show that the solution composition at equilibrium is not uniquely defined by the base content of the gel, but is in addition dependent on the kind of gel that is used. The calcium-sodium results are similar, and somewhat similar observations have been made by Renold who attributed them to inner- and outer-held cations. It would seem likely that the diffusion paths are different in each pure gel, and that a large amount of exchange may take place without a corresponding change in gel structure. No doubt the water content of the gel is an important factor. The ideal case for the study of the exchange reaction would be one in which no structural changes occur in the gel. The practical difficulty is that in experiments of short duration the penetration of the gel may not be constant for a series of different solutions containing the same cations, and that the nature of the gel may change in longer experiments. Although the experiments of Renold often lasted for days, it is evident that the uncertain capacity factor was not thereby eliminated.

Other factors that may affect the available capacity would be a competitive exchange with hydrogen, since aqueous solutions are used, and an exchange with the alumina in the gel. The latter seems a probable explanation of the very high points on some of the exchange curves. Renold states that a $N/2$ cupric chloride solution dissolves alumina from Permutite. The total solution of a part of the gel might so contaminate the solution as to affect the blocking of the diffusion paths in the gel and to alter the pH of the solution. In general one would expect such effects to be of minor importance.

The errors that are introduced by the use of the base content in the place of the cationic content are somewhat lessened by conducting the experiments at constant anionic normality, and by the fact that the relative cationic content of the solution is involved. The compensation, owing to the latter, no doubt accounts for the negligible influence of temperature on the silver-sodium exchange and on the calcium-sodium exchange at high dilution. It may also account for the apparent independence of concentration observed by the writers for the former reaction. However the elimination of a factor by compensation in certain cases does not constitute evidence that the reaction is in general independent of this factor.

The amount of exchange that takes place in a given case is influenced by so many factors that it is difficult to draw conclusions concerning the nature of the true base-exchange reaction, that is, the reaction at constant capacity with the same type of gel material. The writers' results suggest that the composition of the gel is determined by the relative cationic content of the solution if disturbing factors be eliminated. This is in accord with the opinions of Rothmund and Kornfeld (3) and of Verwey (4). The former

consider the reaction as chemical, while the latter treats it as an adsorption process. The effects of temperature are probably small or negligible owing to compensation, and the effects of anionic concentration on uni-univalent exchanges are probably of the same kind.

In the uni-divalent exchanges, the anionic concentration has a marked effect on the total amount of exchange that takes place with salt solutions. Qualitative evidence indicates that this is, at least in part, due to a change in available capacity. The Rothmund and Kornfeld equation as applied to the barium-sodium exchange would be

$$\left(\frac{\text{Na}^2}{\text{Ba} \cdot V} \right)_{\text{Soln.}} = K \cdot \left(\frac{\text{Na}^2}{\text{Ba} \cdot V} \right)_{\text{gel}}^p$$

Na and Ba represent the amounts of these bases in the volume V . From this, it follows that the ratio $\frac{\text{Na}^2}{\text{Ba}}$ for the solution is proportional to the volume of the solution at constant gel composition and capacity. It also follows that the barium in the solution must decrease as the volume increases. The latter deduction is in accord with the observations given in Fig. 3. But if one compares the results at $N/1000$ with the results at $N/4$, at constant gel composition, the ratio $\left(\frac{\text{Na}^2}{\text{Ba}} \right)_{\text{Soln.}}$ is so far from being proportional to the volume of the solution that it is very questionable whether this equation is of the right type. For a gel that contains 25 milli-equivalents of barium, the volume ratio for $N/1000$ and $N/4$ is 250, and the ratio of the two $\left(\frac{\text{Na}^2}{\text{Ba}} \right)_{\text{Soln.}}$ terms is 11.6. Somewhat similar discrepancies were found for gels containing 15 and 20 milli-equivalents of barium. Were it possible to compare these results, for a constant capacity, the two exchange curves would be brought closer together and the discrepancy increased. It would seem likely that the greater part of the differences between these two curves might disappear if a proper correction could be made for the capacities. The curves are much closer together in the case of the barium-sodium reaction than in the other uni-divalent reactions, and a search is being made for a reaction in which they might be even closer together.

In Fig. 4, the lines indicate the usefulness of the equation $P/E'_1 = a + bP$ for the expression of the results at great dilution. The exchange curve must flatten at high solution percentages if it agrees with this equation. Either the equation is not suitable for the whole range or the curve is distorted by some factor such as a variable capacity. For the present, it would seem best to regard the equation as merely a convenient equation for the interpolation of results in certain ranges of solution percentages. The barium nitrate results and Musgrave's silver nitrate results (1) show that it may be useful at low or at high solution percentages in some cases. It does not agree so well with the results that are obtained at the higher normalities such as $N/4$ for the uni-divalent exchange reactions. These results yield curves that change direction and rise rapidly as the solution percentage approaches 100.

Acknowledgment

Professor Beamish suggested the fusion method for the decomposition of calcium Doucil, and lent the writers the necessary apparatus.

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THE BROMINE-SENSITIZED DECOMPOSITION OF CHLORINE MONOXIDE IN GREEN LIGHT¹

BY A. G. BROWN² AND J. W. T. SPINKS³

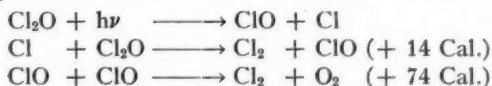
Abstract

Chlorine monoxide undergoes a bromine-sensitized decomposition in light of wave-length 5460 Å. The reaction involves short chains and is accompanied by an appreciable dark reaction. The quantum yield is 4.3 at 19° C. A decrease in pressure occurring near the end of the reaction has been shown to be a photochemical effect, and it is due probably to the bromine-sensitized decomposition of chlorine dioxide formed during the combined light and dark reactions.

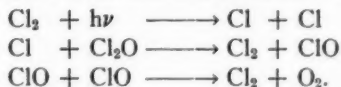
A mechanism similar to that described by Finkelnburg, Schumacher and Stieger for the unsensitized reaction appears to account for most of the observations.

Introduction

The photodecomposition of gaseous chlorine monoxide has been investigated quantitatively by E. J. Bowen (5) and by Bodenstein and Kistiakowsky (4). The rate of decomposition was found to be proportional to the amount of light absorbed, and the observed quantum yield of 2 was the same, irrespective of whether chlorine or chlorine monoxide absorbed the light. The reaction was not affected by the presence of air or oxygen, and chlorine dioxide was shown spectroscopically to be present in increasing amounts as the reaction proceeded. It was suggested that excited molecules of chlorine monoxide or chlorine were responsible for the decomposition. However, Bodenstein and Kistiakowsky (4) and Goodeve and Wallace (12) showed that the absorption spectrum of chlorine monoxide was continuous between 6200 Å and 2300 Å. Thus, following the work of Franck (10) and others it appeared probable that light absorption in this region resulted in the dissociation of the molecule. A reaction mechanism involving such a dissociation and accounting for the observed quantum yield of 2 was proposed by Schumacher and Wagner (25).



The mechanism suggested for the sensitized reaction was:



The gaseous reaction was reinvestigated by Finkelnburg, Schumacher and Stieger (9). They determined the extinction coefficient of chlorine monoxide over the continuous range 6700 to 2200 Å. Four maxima were found in the

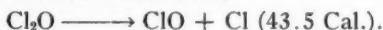
¹ Manuscript received November 16, 1936.

Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon. From part of a thesis by A. G. Brown in partial fulfilment of the requirements for the degree of Master of Science.

² Holder of a bursary under the National Research Council of Canada, 1935-1936.

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region of continuous absorption. The first sharp maximum at 6250 Å (45.5 Cal.) was thought to involve dissociation;



The second and third maxima at 5320 Å and 4290 Å were considered to correspond to dissociation into excited products, ClO and Cl. Absorption in the last broad maximum at 2560 Å (93 Cal.) resulted in dissociation into separate atoms,



Quantum yields were determined for purified dry chlorine monoxide at the wave-lengths 4360, 3650 and 3130 Å. The mean quantum yield for 3650 Å was 3.5 (10° C.) and the mean temperature coefficient 1.12. Chlorine dioxide and higher unknown oxides were shown to be present. The mechanism of Schumacher and Wagner, as outlined, was extended to explain quantum yields greater than 2. Such higher yields were considered to be due to reactions leading to chain formation *e.g.*,



These will be discussed further.

Subsequently, Schumacher and Townend (24) reinvestigated the region of dissociation into atoms. The observed quantum yield of 4.5 at 2500 Å was thought to be due to the primary process



followed by the series of reactions described by Finkelnburg, Schumacher and Stieger.

The thermal decomposition of chlorine monoxide has been investigated by Hinshelwood and Prichard (15), Hinshelwood and Hughes (14) and by Beaver and Stieger (3). Chlorine dioxide again appeared to be formed as an intermediate product, and it seems probable that, apart from the primary action, the mechanisms of the photo and thermal reactions are very similar.

In view of the work already done, the bromine-sensitized decomposition of chlorine monoxide was undertaken. With bromine, green light can be used which produces excited bromine molecules. The reaction of the latter with chlorine monoxide can be studied, and should be of particular interest since very few definite cases of molecular sensitization are known. A comparison with the chlorine-sensitized reaction (where atoms are involved) should also be possible.

Materials

Experimental

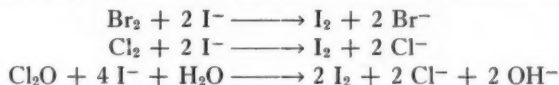
Chlorine monoxide was prepared by passing dry chlorine, either pure or mixed with dry air, over specially prepared mercuric oxide in a water cooled tube. The mercuric oxide was prepared by precipitation from saturated mercuric chloride solution with 50% caustic. After a thorough washing with distilled water, it was collected and dried at 110–120° C. for at least 12 hr. In the preliminary experiments tank chlorine was used, but since the resulting

chlorine monoxide showed a very large dark reaction, the tank chlorine was replaced by chlorine generated from potassium permanganate and hydrochloric acid. Before passing the chlorine over the mercuric oxide, it was purified by bubbling it through potassium permanganate solution, and then dried with concentrated sulphuric acid and phosphorus pentoxide.

The chlorine monoxide from the generating tube was mixed with bromine and drawn into the reaction cell. Since others have shown that the photo-reaction is not affected by air, oxygen or chlorine, no attempt was made at this stage to prepare pure chlorine monoxide.

Methods of Analysis

The composition of the gaseous mixture was found either by analyzing the contents of a bulb of known volume filled at the same time as the reaction cell, or by analyzing the contents of the cell itself. In either case the gas was passed, by means of a stream of dry air, into neutral potassium iodide solution.



After acidifying with a known amount of 0.1 *N* sulphuric acid, the solution was titrated with standard thiosulphate. The titration gave a measure of the total bromine, chlorine and chlorine monoxide. Excess of 0.1 *N* potassium iodate was then added and the iodine titrated.



The difference between this titre and the thiosulphate equivalent of the 0.1 *N* sulphuric acid originally added gave the equivalent of the OH^- produced by the reaction of chlorine monoxide and the iodide solution. Hence, the concentration of chlorine monoxide could be calculated. In some cases the chlorine monoxide concentration was obtained from the total increase in pressure at total decomposition. The bromine concentration may be obtained from the percentage absorption of 5460 Å and an absorption curve for this wave-length. For concentrations of chlorine monoxide sufficient to give an appreciable absorption of 5460 Å it would be necessary to allow for its absorption.

Apparatus and Procedure

Two similar cylindrical cells of Suprax glass, 10 cm. in length and 5 cm. in diameter, with plane ends, were used. The cells and all connecting tubes were immersed in a

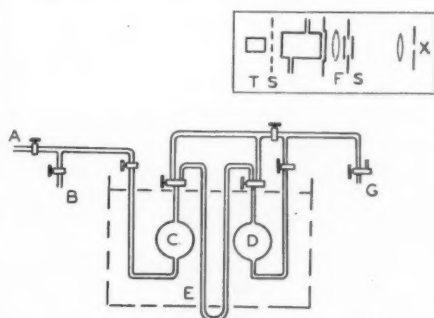


FIG. 1. Apparatus. A, chlorine monoxide inlet; B, bromine inlet; C and D, light and dark reaction cells; E, manometer; G, tube leading to analysis bulbs and water pump. Inset—optical arrangement: T, thermopile; S, S, shutters; F, light filter; X, mercury lamp.

constant temperature bath kept at 19° C. (Fig. 1). The reaction



takes place with an increase in volume. Consequently the course of the reaction was followed by means of a sulphuric acid manometer connected between the cells and read to 0.001 cm. by means of a cathetometer. Taps were lubricated with concentrated sulphuric acid.

Light from a quartz mercury lamp (1.8 amp.) was limited by a 1 cm. diaphragm, and after passing through light filters was made nearly parallel by means of a large semiconvex lens. Then the light was directed, by means of a second convex lens, through a window in the thermostat and into the cell. The whole of the slightly converging beam fell on the surface of a thermopile. A shutter could be interposed between the cell and the thermopile. This allowed readings of light intensity to be made from time to time during the run (Fig. 1, inset).

The wave-length of 5460 Å used in the experiments was obtained by means of a combination of Corning Nonex, heat-resisting yellow glass, 2.8 mm. thick, and a Corning Didymium glass 4.97 mm. thick. This arrangement, together with the light from a mercury arc, gave a source of light of wave-length 5460 Å. The wave-length 3650 Å used in some experiments was obtained by means of a Corning Red Purple Ultra Filter, 3.9 mm. thick.

Energy measurements were made by means of a 2 cm. Moll surface thermopile, stepped down and blackened (23), connected in series with a moving coil galvanometer which had an optical lever of 1.2 m. radius.

The thermopile was calibrated by means of a carbon filament lamp from the Bureau of Standards, Washington, D.C. It was found that 1 mm. scale deflection corresponded to 1.0903×10^{-5} watts per sq. cm.; equivalent to 1.988×10^{15} quanta per minute at 5460 Å and 1.329×10^{15} quanta per minute at 3650 Å, after making a reflection correction of 9.3% (2, p. 1658).

Using the equation $PV = NRT$, an expression may be obtained relating the change in the number of molecules of gas with the movement of the manometer liquid (2, p. 1658). When $V = 186$ cc., $T = 19^\circ \text{C.}$, $P = 715$ mm. and the diameter of the capillary manometer is 1.83 mm.; 1 mm. sulphuric acid $\equiv 8.5 \times 10^{17}$ molecules, a slight correction being made for volume change due to the movement of sulphuric acid in the manometer. Since a change in volume of one mole represents the decomposition of two moles of chlorine monoxide the expression for the quantum yield, γ , reduces to:

$$\begin{aligned} \gamma_{5460} &= \frac{2 \times 8.5 \times 10^{17} \times \text{mm. sulphuric acid per min.}}{1.988 \times 10^{15} \times \text{mm. deflection}} \\ &\equiv 8.55 \times 10^2 \times \frac{\text{slope of rate curve}}{\text{mm. light absorption}} \end{aligned}$$

Results

In several preliminary experiments a fast and unexpected thermal reaction occurred whose rate was considerably reduced when the tank chlorine (used in the preparation of chlorine monoxide) was replaced by chlorine prepared by the interaction of hydrochloric acid and potassium permanganate.

However, when bromine was added to chlorine monoxide a slow dark reaction still took place, and became increasingly faster in subsequent experiments. After a number of runs the reaction cell was cut down and washed out with a few drops of water. The solution so obtained gave tests for ClO_3^- (characteristic diamond-shaped plates of potassium chlorate with potassium chloride solution) and ClO_4^- (typical crystal clusters with 2% brucine in dilute acetic acid). These results indicate the presence of Cl_2O_6 which reacts with water according to the equation.



By cleaning the cell at intervals the thermal reaction rate was kept quite low compared to the rate of the photo reaction (0 to 15%). The true rate of the photo reaction was determined by subtracting the mean rate of the thermal reaction (before and after the experiment) from the total reaction rate during insolation. A typical pressure-time curve is shown in Fig. 2 (a).

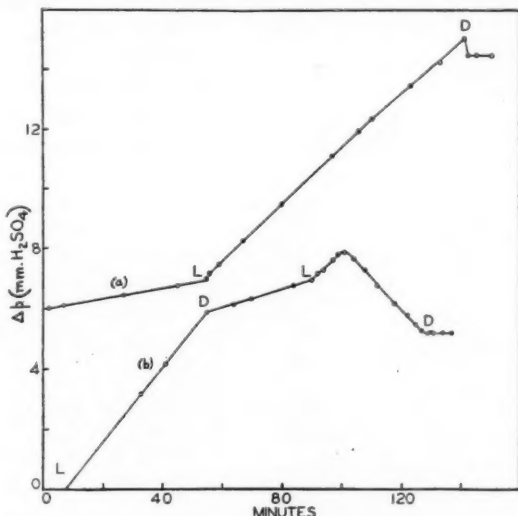


FIG. 2 Typical pressure-time curves.

On insolation there was a small Budde effect, after which the pressure increased steadily. When the light was cut off an inverse Budde effect was produced, and the pressure then increased more slowly owing to the small thermal reaction. Upon re-insolation the increase in pressure continued at the former rate.

Toward the end of the reaction ($\text{Cl}_2\text{O} < 0.25\%$) an unexpected effect was observed. In a period of less than five minutes, the normal pressure increase changed over into a pressure decrease. On cutting off the light, the pressure remained constant. This indicated that the effect was photochemical. The pressure decrease continued on further insolation and was thought to be due

to a condensation of a relatively non-volatile substance such as Cl_2O_6 on the walls of the vessel (Fig. 2 (b)). After a further period of insolation the pressure began to increase again, and it continued to increase until all the chlorine oxides had decomposed. The effect was first observed with light of wave-length 5460 Å and mixtures containing bromine. A similar effect was observed for bromine-free mixtures and the wave-length 3560 Å*.

From the rate of decomposition (as measured by the slope of the pressure-time curve) and the number of absorbed quanta, the quantum yield was calculated. While the above-mentioned irregularities would seem to make

TABLE I
QUANTUM YIELDS FOR THE BROMINE-SENSITIZED
REACTION AT 5460 Å

Chlorine monoxide-bromine mixtures (plus chlorine and dry air) at 19° C.
Total pressure, 710 mm. of mercury.

Chlorine monoxide by volume, %	Light absorbed (by bromine), %	Quantum yield
0.32	57.0	5.2
0.35	19.3	4.1
0.59	58.2	4.7
0.70	51.6	3.5
0.91	58.6	4.0
1.02	61.0	4.4
1.2	65.5	4.1
1.39	66.1	3.9
2.3	22.2	5.3
3.1	23.1	4.3
5.0	60.0	4.4
5.5	31.0	4.8
6.3	37.4	4.2
		Mean 4.3

the exact magnitudes of the quantum yields somewhat uncertain, the values obtained in the early period of the reaction were all approximately equal to 4 over a range of concentrations of chlorine monoxide from 0.35 to 5.0% and bromine from 1 to 6% (from 20 to 75% absorption of 5460 Å). The mean value of γ_{5460} for the sensitized experiments was 4.3, the possible error being about 10% (Table I).

Quantum yields for the unsensitized photodecomposition of chlorine monoxide were also determined. A dark reaction again appeared as a variable and complicating factor, and the mean value of γ_{3650} for the unsensitized reaction was found to be 5.3 at 19° C. This is somewhat higher than the value obtained by Finkelburg and co-workers (9).

Their value $\gamma_{3650} = 3.5$ at 10° C. and a temperature coefficient 1.12 leads to $\gamma_{3650} = 4$ at 19° C. It is possible that the difference may be due either to the dark reaction or to the low concentration of chlorine monoxide.

The ratio $\frac{\gamma_{3650} \text{ (unsensitized)}}{\gamma_{5460} \text{ (sensitized)}} = \frac{5.3}{4.3} = 1.2$. From the values of γ for different wave-lengths in Schumacher's paper (9, p. 145) one can estimate that for the unsensitized reaction, $\frac{\gamma_{3650}}{\gamma_{5460}} = 1.3$. Therefore the ratio $\frac{\gamma_{5460} \text{ (sensitized)}}{\gamma_{5460} \text{ (unsensitized)}} = 1.08$.

While the accuracy is not very great, one can safely say that the quantum yields for the sensitized and unsensitized reactions are practically equal. The equality of the quantum yields obtained in these experiments suggests

* Finkelburg and co-workers (9) record a sharp rise in pressure at the end of one of their experiments.

that, apart from the primary act of light absorption, the sensitized and unsensitized reactions have essentially similar mechanisms. The reaction thus shows a close resemblance to the chlorine-sensitized decomposition of chlorine monoxide (4) and the bromine-sensitized decomposition of chlorine dioxide (27).

Experiments were attempted with water covering the bottom of the reaction cell, using bromine and chlorine monoxide mixtures. An extremely rapid increase in pressure was observed in the dark, the rate decreasing slightly on insolation with light of wave-length 5460 Å. Because of the magnitude of the dark reaction, further investigation in this direction seemed unprofitable.

Discussion

Primary Effect of Light Absorption

While 5460 Å is well within the continuum for chlorine monoxide, the extinction coefficient at this wave-length is very low. In a preliminary experiment with chlorine monoxide at a partial pressure of 304 mm. of mercury, the absorption of 5460 Å by a 10 cm. thickness was 18.6%. This is in good agreement with the value given by Goodeve and Wallace (12), and shows that, in the sensitized experiments, even the highest concentrations of chlorine monoxide used (40 mm. of mercury) would absorb less than 3% of the incident light at 5460 Å. In most experiments the absorption of the incident light by chlorine monoxide would be less than 1%. This was verified by direct measurement. Consequently, in the bromine-sensitized reaction the light is being absorbed almost exclusively by the bromine.

Since the mixture contains chlorine the possibility of BrCl formation has also to be considered even at the beginning of an experiment. The equilibrium constant K for the reaction $2\text{BrCl} = \text{Br}_2 + \text{Cl}_2$ is 0.107 at 28° C. (30). If the heat of formation given by Jost (16) is used, the value of K at 19° C. is 0.111, which corresponds to the formation of a relatively large percentage of BrCl, the percentage naturally depending on the concentrations of bromine and chlorine.

According to Vesper and Rollefson (30), bromine and chlorine react comparatively slowly in the dark, but this result is contradicted by Jost (17) and by Brauer and Victor (6) who find a rapid reaction. The reaction rate is accelerated by light (absorption in the band and continuous regions being equally effective) and the photoreaction has a quantum yield of about 10^3 . It is of course quite possible that the reaction may be strongly inhibited by chlorine monoxide.

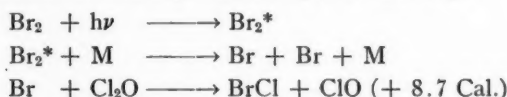
Gray and Style (13) mention that the transmission of 5460 Å by mixtures of bromine and chlorine is unaffected by insolation with 5460 Å, and that the extinction coefficient of BrCl is very small compared to that of bromine at the same wave-length ($\frac{\alpha_{\text{BrCl}}}{\alpha_{\text{Br}_2}} = \frac{1.2}{29.6}$ at 5460 Å). Thus, in these experiments the light is being absorbed almost exclusively by bromine.

The main continuum for bromine begins only at 5107 Å, and it is therefore evident that the primary process of light absorption at 5460 Å results in the formation of excited bromine molecules. It should perhaps be mentioned that there is a faint underlying continuum extending to at least 6400 Å, and that absorption in this continuum would lead to dissociation into normal atoms (1,7). However, from the relative intensities of the underlying continuum and the main band system, it appears probable that the fraction of bromine molecules dissociating directly, as a result of light absorption at 5460 Å, is small. The fact that 5460 Å excites fluorescence in bromine (20) also supports the hypothesis that excited bromine molecules are formed.

There is of course the further possibility that excited bromine molecules dissociate on collision with another bromine molecule or with a foreign molecule. Rabinowitch and Wood (21, 22) give experimental proof that, in the case of iodine, all excited iodine molecules dissociate because of collisions with foreign molecules. They also consider that the observations of Jost on the bromine-hydrogen reaction in the band and continuous regions of the bromine spectrum make it probable that a great number of primarily excited bromine molecules dissociate into atoms by collisions with hydrogen and bromine molecules. The reactions of bromine with ozone (26), platinum (29), cyclohexane (18), chlorine dioxide (27) and chlorine (6), show a similar behavior.

Mechanism of the Sensitized Photoreaction

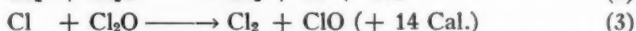
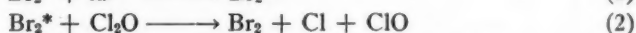
If the secondary production of bromine atoms is postulated, the first part of the reaction can be represented by the following:



ClO would then react further with chlorine monoxide (see below). The ratio of BrCl formed to chlorine monoxide decomposed would be in the ratio 2 : γ, i.e., about 2 : 4 in the authors' experiments. Since the extinction coefficient of BrCl differs from that of bromine at 5460 Å (see above), an increase in light transmission at this wave-length would be expected. Actually none was observed, but the situation is complicated by the fact that BrCl decomposes into bromine and chlorine to form an equilibrium mixture. If this equilibrium were rapidly established (possibly accelerated by bromine atoms), the net removal of bromine as BrCl would not be as great as suggested by the above equations. The evidence in favor of the reaction proceeding by way of bromine atoms is thus rather inconclusive.

The other possibility is that the primarily excited bromine molecules collide with a chlorine monoxide molecule and decompose it. The decomposition of chlorine monoxide requires 43.5 Cal. and the quantum at 5460 Å corresponds

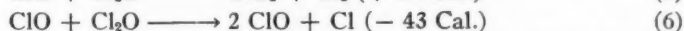
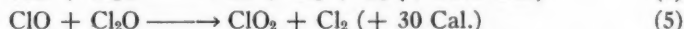
to 52 Cal. Hence a decomposition in this manner is energetically possible and may be represented by the following equations:



It is of course possible that an excited chlorine monoxide molecule is first formed and then splits up or reacts with another chlorine monoxide molecule. However, the first possibility would be indistinguishable from Reaction 2, and the similarity of the sensitized and unsensitized reactions makes the reaction $\text{Cl}_2\text{O}^* + \text{Cl}_2\text{O} \longrightarrow 2 \text{Cl}_2 + \text{O}_2$ unlikely.

If the above mechanism is accepted, the observed quantum yields force one to conclude that energy exchange between bromine and chlorine monoxide molecules is quite specific, and takes place at practically every collision. At the same time the probability of an excited bromine molecule losing its energy on collision with foreign molecules such as oxygen or nitrogen must be small. A similar specific energy transfer occurs in the bromine-sensitized decomposition of chlorine dioxide (27). The importance of the nature of the colliding partner for deactivation of molecules activated by light is discussed by Franck (11), who concludes that collisions will be particularly efficient for dipoles and radicals. It is perhaps significant that chlorine monoxide has a dipole moment of 0.78×10^{-18} (28), while oxygen and nitrogen have zero dipole moments.

Quantum yields greater than 2 might result from the following reactions suggested by Finkelnburg, Schumacher and Stieger (9):



Of these, Reaction 6 is certainly infrequent. Reaction 5 has been shown to take place in the unsensitized reaction, and it is probably also responsible for the end effects in the sensitized reaction. Reaction 4 would provide the chain mechanism necessary to account for the observed quantum yields.

The chains must be terminated rather rapidly by the following reactions, but it is not yet possible to estimate their relative importance.

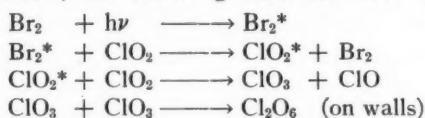


The Pressure Decrease

There remains to be explained the decrease in pressure observed at the end of the reaction. This was proved to be a photoeffect and the experiments also suggested that some substance was separating out on the walls. Since chlorine dioxide is formed (Reaction 5), it seems probable that the bromine-

sensitized decomposition of this oxide takes place. This reaction has been shown to occur with a decrease in pressure at 16° C. owing to the separation of Cl_2O_6 on the walls (27). That this is the cause of the decrease in pressure observed at the end of the authors' experiments is supported by the chlorate and perchlorate formation described previously, and by the shape of the curves obtained on further insolation. It seems necessary to assume, however, that chlorine dioxide accumulates during the first part of the reaction, and that there is a preferential decomposition of chlorine monoxide as long as it is present in appreciable quantity†.

Since the wave-length 5460 Å does not come within the predissociation region for chlorine dioxide, the following reactions have been suggested:



Other reactions of ClO and ClO_2 may also take place. The subsequent increase in pressure is due to the photodecomposition of Cl_2O_6 (27).

It is of particular interest to note that while the secondary production of bromine atoms is not entirely excluded, the bulk of the evidence favors sensitization by excited bromine molecules. Examples of reactions that are definitely of this type are extremely rare for unsensitized reactions†† and almost as rare for sensitized reactions, particularly where the sensitizer is a molecule.

Whereas excited atoms (mercury atoms, for example) usually sensitize a reaction by transferring their energy to molecules or atoms by collisions of the second kind, most molecular sensitizers play an active chemical role, the original sensitizing molecules being regenerated during the course of the reaction.

From the foregoing it is seen that, apart from the primary process of light absorption, the sensitized and unsensitized reactions have essentially similar mechanisms. The photoreaction is rather complicated and the unsensitized reaction needs to be investigated further before any more work on the bromine-sensitized reaction is undertaken.

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† Compare the observations of Dickinson and Jeffreys (8) on the decomposition of chlorine monoxide in solution.

†† Compare the remarks of Norrish and Kirkbride (19).

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THE VARIATION OF THE SULPHUR CONTENT OF WOOL¹

BY P. LAROSE² AND A. S. TWEEDIE³

Abstract

The results obtained by other investigators which have a bearing on the variability of the sulphur content of wool are reviewed briefly. The variability of the sulphur content is discussed on the basis of the various factors that might affect it.

The effect of light is appreciable and is a very important one. Any sulphuric acid formed by the action of light, or present owing to some other cause, is difficult to remove by ordinary washing. The effect of boiling water is small. Kempy fibres contain less sulphur than non-kempy fibres of the same wool. The root portions of fibres have a higher sulphur content than the tip portions, while middle portions have intermediate values.

The writers' results and those of other investigators which are reproduced do not allow of any definite relation being drawn between sulphur content and fineness.

Introduction

The variability of the sulphur content of wool has engaged the attention of a number of investigators interested in the composition of wool. The diverse and often contradictory results obtained by various workers have resulted in differences of opinion regarding the extent of the variation in sulphur content and its relation to those factors capable of influencing it. These factors can be divided into internal and external, the internal factors being those that determine the process by which the wool fibre is formed in the follicle, whereas the external factors are those that act on the wool fibre outside the follicle. Differences of sulphur content between wools of various breeds, between wools of different fineness or between kempy and non-kempy wool would be due to the first-mentioned factors. The most important factors are probably the composition of the feed and the plane of nutrition. Among the external factors are the action of light and any action that the suint, wax or other substances present in the raw wool may exert.

Since in actual practice the effect exerted by the external factors on the various wools would vary in degree, it is difficult to correct for it when attempts are made to correlate the sulphur content with the internal factors. This may account for some of the differences in results obtained by various investigators.

The writers were interested in the variability of the sulphur content of Canadian wools, and they used the method described by Larose and Tweedie (10). They were interested also in carrying out sulphur determinations on a number of these wools and to a limited extent in verifying relations found by previous investigators.

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Effect of Light Exposure

The decomposition of wool by light with the resulting decrease in sulphur content has been recorded. Barritt and King (3) exposed wool to the light of a quartz lamp for 80 to 100 hr. and found losses in sulphur varying from 3.7 to 5.0% of the original sulphur content, but these losses were larger (9.0 to 13.1%) when the wool was washed, after exposure, in a 0.001 *N* sodium hydroxide solution. Barritt and King showed that this dilute alkali treatment did not affect the sulphur content of normal wool. Mossini (12) reported a loss of 2.4% after exposing a sample of Australian wool to sunlight for 50 hr., but the losses were very much greater when the wool was subsequently treated with various solutions. Treatment in lime water after exposure gave the greatest loss (84%). This extraordinarily large loss is due, no doubt, not only to the action of light but also to that of the lime water on the wool.

Tests of a similar nature were conducted by the writers on samples of low $\frac{1}{4}$ Leicester wool that were exposed, one uncovered and the other under glass, for 132 hr. in sunlight. The results are given in Table I.

TABLE I
EFFECT OF EXPOSURE TO LIGHT ON SULPHUR CONTENT
Low $\frac{1}{4}$ Leicester wool. Original sulphur content, 3.47%

Treatment	Sulphur, %	Loss, %
Sample under glass for 132 hr. and exposed to sunlight (<i>A</i>)	3.30	4.9
<i>A</i> washed in several changes of water and one hour in 0.001 <i>N</i> sodium hydroxide	3.10	10.7
Sample uncovered and exposed to sunlight for 132 hr. (<i>B</i>)	3.30	4.9
<i>B</i> washed in several changes of water and one hour in 0.001 <i>N</i> sodium hydroxide	2.85	18.2

These results show changes of the same order as those reported by Barritt and King. The smaller loss in sulphur content of the wool covered by glass during exposure is due probably to a reduction in intensity of the light of shorter wave-lengths in passing through the glass.

Another sample that had been exposed for 96 hr. in a fugitometer but that was not subsequently washed with dilute alkali showed a loss too small to be significant, probably owing to a different distribution of light energy and to the unfavorable condition of low humidity obtaining at the time of test.

Effect of Absorbed Sulphuric Acid.

In connection with the test on exposure to light, an experiment was carried out to determine the extent to which any sulphuric acid in the wool was removed by the ordinary water rinsing. A sample of wool was treated with a 1% sulphuric acid solution according to the procedure adopted by Wilkinson and Tyler (16, p. 370) in their work on the absorption of acids by wool. The

original sulphur content of the wool was 3.58%. After the acid treatment the value found was 3.76%, corresponding to an "acid retained" value of 0.54%, a value somewhat lower than the 0.7% reported by Wilkinson and Tyler. The wool was subjected to a further rinsing in running warm distilled water of pH 5.5 for six hours, and this reduced the sulphur value to 3.69%, corresponding to an acid retention of 0.33%. It is, therefore, difficult to remove all sulphuric acid by water alone, and this should be borne in mind when a determination is made of the sulphur content of wool suspected of containing sulphuric acid.

Effect of Boiling Water

It has been observed by Clayton (8) that when wool is heated in boiling water, hydrogen sulphide is given off, although the quantity is very small and the evolution is said to cease after a short time. The extent of such evolution was determined by analyzing for sulphur content, before and after the treatment, a sample of Welsh wool that was boiled for five two-minute periods, the water being changed between each boiling. The sulphur was also determined for a sample that had been subjected to a further boiling for one hour. The results are given in Table II.

TABLE II
EFFECT OF BOILING ON SULPHUR CONTENT OF WOOL
Original sulphur content, 4.12%

Treatment	Sulphur, %
After boiling five two-minute periods	4.07
After boiling one hour more	4.04

These figures indicate that there is an appreciable loss of sulphur on boiling with water, but that most of this loss occurs during the initial stages, in confirmation of previous observations.

Sulphur Content of Kempy Fibres

That kempy fibres have a lower sulphur content than non-kempy fibres from the same wool has been shown by Barritt and King (2), who reported values of 3.82, 3.33 and 3.24% for fine non-kempy wool, coarse kempy wool and kemps, respectively, in a sample of Black Face wool. They used these figures to show (4) that the medulla from kempy fibres was free of sulphur. Bekker and King (5) worked with porcupine quills and carried out a partial separation of the cortex from the medulla. By direct determination they found a lower sulphur content in the medulla than in the cortex. That the medulla showed an appreciable sulphur content was attributed to incomplete separation of the cortex from the medulla. Staining methods, applied to cross sections of wool fibres as well as porcupine quills, seemed to show the absence of sulphur in the medulla. Jordan-Lloyd and Marriott (9) found that the medulla could be separated from the cortex in goat hair by treatment with 4*N* sodium hydroxide solution, and they took advantage of this to carry out sulphur determinations in the cortex and medulla separately. A sulphur content of 3.60% was found for the cortex and 0.23% for the medulla.

These results show that if the medulla is not entirely free of sulphur, its sulphur content is at least much lower than that of the cortex, and they explain why kempy fibres should be found to have a lower sulphur content.

Table III gives the results obtained by the writers which are in agreement with those previously reported.

The agreement between individual determinations on the samples listed in Table III was not so good as that usually obtained. This was to be expected in view of the wide variation in the kempiness of the fibres.

TABLE III
SULPHUR CONTENT OF KEMPY FIBRES

Sample	Sulphur, %
Original wool	3.45
Kempy fibres from original wool	3.36
Non-kempy fibres from original wool	3.55
Kempy fibres from fine locks in original wool	3.56
Non-kempy fibres from fine locks in original wool	3.68
Kempy fibres from coarse locks	3.34

Variation Along the Fibre

The wool fibres have been divided at times into two or three distinct portions, generally into base, middle and tip portions in order to determine the variation of the sulphur content along the fibres. This variation, as found by various investigators, was not always in the same direction. Bonsma (6) found the greatest sulphur content in the root portion and the smallest in the middle portion. He attributes variations found along the length to differences in nutrition during the periods of growth of the various portions.

Barritt and King (3) found that the sulphur content of the tip portions was generally greater than that for the rest of the fibre. They suggest that the greater sulphur content may be due to a more active sulphur-stimulus immediately after shearing. The protective action of wool grease in the denser fleeces is mentioned as a possible factor, for in two open fleeces the sulphur value for the tip portion was not appreciably higher than that for the remaining portion of the fibres.

The writers determined the sulphur content of the root, middle and tip portions of two New Zealand wools. The results are given in Table IV.

TABLE IV
VARIATION OF SULPHUR CONTENT ALONG THE FIBRE

Sample	Sulphur, %	Sample	Sulphur, %
New Zealand 36's		New Zealand 60's	
Root	3.33	Root	3.67
Centre	3.08	Centre	3.57
Tip	3.00	Tip	3.47
Original whole fibres	3.16	Original whole fibres	3.55

In both samples there is a gradation from root to tip, the root portion having the greatest sulphur content. It is reasonable to suppose that the smaller figures obtained for the tip portions are due to decomposition by exposure to light. It is true that in many cases reported the tip did not have the smallest sulphur content, but in such cases the effects can very well be explained by differences in plane of nutrition during the growth period. A better feed was probably more than sufficient to balance the loss due to the light effect. Atmospheric conditions, the amount of wax, suint, and dirt are all factors that would influence the decomposition of the wool, and it is to be expected that wide variations in the effect of light would be found.

Variation with Fineness

It has been stated at various times that fine wool contains more sulphur than coarse wool, *e.g.*, by Mullin and Hunter (13, p. 746) in reporting on the work of Takeda, and by Barker (1, p. 36). However, the evidence available is such that no definite conclusion can be reached. Some of the values quoted would indicate that the finer the wool the greater the sulphur content, but in many cases the results show no such relation. The lack in agreement is to be expected when it is remembered that fineness is not the only factor determining the sulphur content of wool. Comparison can be justified only when other conditions affecting sulphur content are equal.

Some of the evidence with respect to the relation between fineness and sulphur content will be reviewed briefly.

Barritt and King (2, p. 394), who were probably the first to carry on a fairly extensive study of the sulphur content of wool and similar fibres, quoted a value of 3.36% sulphur for the fine fibres, and 3.03% for the coarse fibres of Turkey mohair. The values given by Bonsma (6) also show, on the whole, that the smaller sulphur content corresponds to the coarser wool. A certain relation between handle and the sulphur content is also indicated by the values given. The best handling wools in general have a greater sulphur content than those with a poor handle. This has been pointed out by Sidey (15) who also investigated the relation between spinning property and sulphur content, and found that the greater sulphur content corresponded to the better spinning fibres as determined by their *A/B* contour ratio, in which *A/B* represents the ratio between major and minor axes of the elliptical cross section of the fibres.

Rimington (14) reported some results that also show coarse wool to contain less sulphur than the finer wool.

Mossini (12) has analyzed wools of various qualities and claims that his results show a direct relation between quality of the fibre and sulphur content. His figures are reproduced in Table V.

TABLE V
RESULTS OF MOSSINI

Wool	Sulphur, %
Australian AAA	3.70
Australian AA	3.28
Australian A	3.46
Buenos Ayres A/B	3.46
Buenos Ayres B	3.82
Buenos Ayres C	3.28
Buenos Ayres D	3.08
Capo AA	3.62
Capo A	3.30
Bahia A/B	3.22
Bahia B	3.31
Bahia C	3.27
Bahia D	3.74
Puglia C	2.92
Puglia D	3.26

It will be noted that the values for the Australian *A* and Buenos Ayres *A/B* qualities do not fall in the proper places if the finer qualities are to be greater in sulphur content. The Bahia finest wool has the smallest sulphur content, and the poorer quality has the greatest sulphur content of the group, while the Puglia wools are also in the wrong order. The evidence furnished by these figures is, therefore, very contradictory.

The results obtained by Winton and Edgar (17) are reproduced in Table VI in order of decreasing sulphur content. It is difficult to show any relation since the quality or fineness of the wools analyzed is not stated. However one may judge fairly closely from the breed.

TABLE VI
WINTON AND EDGAR'S RESULTS

Breed	Sulphur, %	Breed	Sulphur, %
Delaine Merino	3.76	Southdown I	3.33
Merino B type	3.63	Shropshire II	3.33
Rambouillet	3.59	Oxford	3.34
Southdown II	3.55	Columbia	3.33
Dorset	3.53	Hampshire I	3.19
Shropshire I	3.50	Romney	3.02
Hampshire II	3.49	Cotswold II	3.00
Leicester	3.45	Cotswold III	2.99
Corriedale	3.35	Lincoln	2.92
Cotswold I	3.35		

In Column 1 of Table VI the breeds are roughly in the order of decreasing fineness, the Corriedale being probably the only one out of place. In Column 3, the order is also very good except perhaps for the Oxford and Columbia samples. However, if the two columns are studied together the relation is disturbed, although the finest wools still remain at the top. It is difficult to surmise why the wools fall into two distinct groups.

Marston (11) has reported results to show that "the sulphur content of wool keratins from widely different sources were found identical within experimental error . . .". Indeed, the total variation between the coarsest wools (Leicester and Lincoln) and the finest wool (Merino 70-74's) is only 0.07% actual sulphur. In view of the wide range of qualities covered, this difference is not significant.

Marston reported his sulphur values to the third decimal place. This is not warranted in view of the experimental error which by Marston's own statement must be of the order of 1%. The third decimal figure thus becomes meaningless, otherwise there would be a regular decrease of sulphur content as the wool becomes coarser, as his results reproduced in Table VII show.

TABLE VII
MARSTON'S RESULTS

Breed	Sulphur, %	Breed	Sulphur, %
Merino 70-74's	3.585	Polwarth 60	3.535
Merino 70	3.585	Merino 58	3.546
Merino 64	3.581	Polwarth 56	3.541
Merino 64	3.580	Shropshire 56	3.530
Merino 64	3.560	Leicester	3.523
Merino 60	3.562	Lincoln	3.521

Bonsma and Joubert (7) have tested a large number of samples taken from various parts of fleeces of Merino sheep of known history and maintained under definite conditions of nutrition, thereby reducing the number of variable factors. Their results show absolutely no correlation between sulphur content and fineness. It is unfortunate that similar experiments have not been carried out with other breeds, as the Merino fleeces are generally fairly uniform in quality. Table VIII, in which the wools have been grouped into classes of varying fineness, summarizes Bonsma and Joubert's results.

TABLE VIII
SUMMARY OF BONSMAS AND JOUBERT'S RESULTS

Diameter range, μ	Mean % sulphur
18.0 - 18.9	3.40
19.0 - 19.9	3.34
20.0 - 20.9	3.42
21.0 - 21.9	3.35
22.0 - 22.9	3.36
23.0 - 23.9	3.44
24.0 - 24.9	3.46
25.0 - 25.9	3.44
26.0 -	3.44
	Av. 3.40

The mean sulphur content for each class varies very little and may be considered constant within experimental error. How much the limitation of the tests to one breed has contributed to the constancy of the figures is difficult to say with our present knowledge.

The writers have analyzed a number of samples from various breeds. The results, given in Table IX, show no relation between fineness and sulphur content.

TABLE IX
WRITERS' RESULTS FOR VARIOUS BREEDS

No.	Breed	Quality	Sulphur, %
1	Suffolk	56's (G)	3.92
2	Oxford	{ 50's (G)	3.85
3	Cheviot	{ 44's (L)	3.83
4	Southdown	48's (G)	3.79
5	Suffolk	56's (G)	3.77
6	Merino	48's (L)	3.75
7	Romney	64's (L)	3.70
8	Merino	46's (G)	3.64
9	Suffolk	64's (L)	3.54
10	Leicester	44's (L)	3.50*
11	Hampshire	40-44's (G)	3.20
		56's (G)	

*Mean of two samples.

Nos. 1, 2, 5, 9, 10 and 11 were samples picked from sheep belonging to one experimental flock and maintained under the same conditions regarding environment and feed. Samples 2, 5 and 9 were clipped from the shoulder, while 1, 10 and 11 were samples representative of the grade chosen from the fleece by the grader. Nos. 4 and 7 belonged to another flock and were also representative samples. The remaining samples belonged to isolated cases. Sample 6 was a shoulder sample, while 3 and 8 were representative samples. The quality assigned to the wool for the samples marked (G) is that given by the grader, while for those marked (L) the quality was determined from fibre diameter measurements carried out in the laboratory. In the case of Sample 2, the grader had assigned a higher quality to the fleece as a whole than that determined on the smaller sample tested. Sample 9 was made up of black and partly black fibres picked from Sample 1.

Another series of determinations was carried out on carefully sorted New Zealand wool samples picked out in one particular mill. The results obtained on these wools are given in Table X. The fineness is that given by the wool sorter.

TABLE X
VARIATION OF SULPHUR WITH FINENESS

Fineness	Sulphur, %	Mean, %
36's	3.16	3.16
38's	3.20	
40's	3.12	
44's	3.35	3.39
46's	3.43	
48's	3.09	3.07
50's	3.05	
54	3.31	3.30
56	3.33	
58	3.27	
60	3.35	3.30
64-70	3.67	

These figures show some correlation between fineness and sulphur content in that the 44-46's wool is greater in sulphur content than the 36-40's qualities, and the 48-50, 54-58, 60, 64-70's qualities have an increasing sulphur content. However, the relation is spoiled by the discontinuity occurring between the 44-46's and the 48-50's groups. As the types of wool comprising the various qualities are not known, it is impossible to give an explanation for this break.

From all this accumulated evidence there is some indication that the sulphur content varies with fineness, but no definite relation can be enunciated. The best that can be said is that the finer wools are generally associated with a high sulphur

content and the coarsest wools with a low sulphur content. If there is a relation between fineness and sulphur content, it is probably hidden in most cases by the disturbing influence of other factors, such as inheritance effects, nutritional conditions, climatic conditions. The effect of light has already been shown to be important, and it is doubtful whether concordant results can ever be obtained as long as this effect is neglected. In order to eliminate its influence, comparison on the root portions only of fibres should probably be made. In this connection microdeterminations of sulphur made on a few fibres whose diameters have been measured would be very desirable, and the combustion method would be very suitable for this purpose.

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CONTRIBUTIONS TO THE BIOCHEMISTRY OF BROMINE

II. THE BROMINE CONTENT OF HUMAN TISSUES¹

By A. H. NEUFELD²

Abstract

A study of the bromine content in human tissues was made by the method outlined in Part I of this series. In many cases, total halogen determinations were made on the same material. The results suggest the following conclusions:

Bromine is a constituent of all human tissues. The amounts found in the same tissue show definite variations.

No evidence could be found to support the view that bromine is concerned with pituitary function. The thyroid contains amounts of bromine slightly greater than the amounts found in blood. While functional significance cannot be excluded, it has not been ascertained.

No definite relation was found to exist between the distribution of bromine and chlorine in human tissues.

Introduction

The work reported on in Part I of this series has been extended to the study of bromine in human tissues. The values in the literature show wide variations, largely owing to inaccuracy of the methods used. This cause of error was fully discussed in the first paper (15). Because of such inaccurate methods, theories ascribing, for example, a special function to the pituitary (24, p. 58) in bromine metabolism are deemed fallacious.

Experimental Results

In the present paper, results are given for the available tissues of five persons. Two were killed accidentally. One was a boy of 14 years, Case 1, and the other a woman of 50 years, Case 2. They were apparently in normal health at the time of death. Of the others, a man of 70 years and a man of 71 years, Cases 3 and 4 respectively, died from heart failure (cardiac myocarditis). A woman of 50 years, Case 5, died from cerebral haemorrhage. No definite lesions were found in any of the tissues examined in the last three cases.

The results obtained are given in Table I. All bromine analyses, with three exceptions, were carried out in duplicate, and agreement similar to that shown in the analyses recorded in the first paper of this series was obtained. Only the mean results, therefore, are given.

Ucko (21), in a recent paper, claimed that there is a definite relation between the bromine and chlorine contents of mammalian tissues, while Leipert (10) has claimed that such a definite ratio also exists in blood, urine and gastric juice. The writer has analyzed a large number of tissues for total halogen, using Van Slyke's method (20). The results (means of duplicate determinations) are given in Table I, expressed in terms of chlorine.

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In the last column of Table I are given the equiatomic distribution ratios of bromine and chlorine in terms of chlorine. The necessary corrections for iodine have not been made, except for the thyroid material. Since the iodine contents of other tissues are extremely small, the values taken for chlorine are sufficiently accurate.

TABLE I
CONTENT OF WATER, BROMINE, AND TOTAL HALOGEN (AS CHLORINE) IN HUMAN TISSUES

Tissue	Water content, %	Bromine		Total halogen (Cl)		Ratio Br/Cl $\times 10^3$	Equiatomic distribution Br/Cl $\times 10^3$
		Dry tissue, mg. %	Fresh tissue, mg. %	Dry tissue, %	Fresh tissue, %		
Case No. 1							
Adrenal	64.13	0.6	0.22	—	—	—	—
Bile (bladder)	87.05	2.7	0.35	—	—	—	—
Blood	77.10	3.35	0.765	1.089	0.249	3.07	1.50
Bone (rib)	67.83	0.85	0.275	0.362	0.116	2.37	1.05
Cerebellum	79.76	1.15	0.235	0.426	0.086	2.73	1.21
Cerebrum	77.38	0.6	0.135	—	—	—	—
Gall bladder	81.52	1.2	0.22	—	—	—	—
Heart	80.27	0.7	0.14	0.362	0.071	1.97	0.81
Large intestine	72.73	2.05	0.56	—	—	—	—
Small intestine	81.81	1.05	0.19	—	—	—	—
Kidney	77.73	1.5	0.335	0.883	0.197	1.71	0.76
Liver	76.71	0.55	0.13	0.655	0.152	0.86	0.38
Lung	81.54	1.8	0.33	—	—	—	—
Muscle	76.57	1.25	0.295	0.248	0.058	5.09	2.26
Pancreas	74.63	1.95	0.495	—	—	—	—
Prostate	82.48	1.6	0.28	—	—	—	—
Spleen	79.81	2.2	0.445	—	—	—	—
Stomach	80.47	4.3	0.84	1.323	0.258	3.26	1.45
Testes	83.97	1.6	0.255	1.340	0.215	1.19	0.53
Thymus	80.82	0.7	0.135	—	—	—	—
Thyroid	76.74	10.0	2.325	0.679	0.158	14.72	7.08
Case No. 2							
Blood	85.11	4.15	0.62	1.779	0.265	2.34	1.04
Bone (rib)	52.90	0.6	0.28	0.205	0.096	2.92	1.29
Cerebellum	78.76	0.6	0.13	0.484	0.103	1.26	0.56
Cerebrum	82.58	0.15	0.025	0.470	0.082	0.30	0.14
Heart	71.19	1.0	0.29	0.439	0.126	2.30	1.02
Small intestine	60.16	1.85	0.74	0.477	0.190	3.89	1.77
Kidney	73.46	3.1	0.82	0.926	0.246	3.33	1.48
Liver	72.96	0.15	0.04	0.389	0.105	0.38	0.17
Lung	82.45	2.65	0.465	1.450	0.254	1.83	0.81
Medulla—lower*	73.02	0.7	0.19	—	—	—	—
Medulla—upper†	70.78	0.6	0.175	0.342	0.100	1.75	0.78
Muscle	64.96	1.6	0.56	0.268	0.094	5.86	2.65
Pancreas	66.95	1.35	0.445	0.461	0.152	2.93	1.30
Pituitary	80.44	0.6	0.12	—	—	—	—
Spleen	77.47	1.0	0.225	0.616	0.139	1.62	0.72
Stomach—cardiac	73.35	2.3	0.61	0.757	0.202	3.02	1.34
Stomach—pyloric	68.55	1.7	0.535	0.509	0.160	3.34	1.49
Thyroid	77.77	8.0	1.78	0.660	0.147	12.11	5.68
Uterus	78.91	4.0	0.84	1.068	0.255	3.76	1.67

TABLE I—*Concluded*
 CONTENT OF WATER, BROMINE, AND TOTAL HALOGEN (AS CHLORINE) IN HUMAN TISSUES

Tissue	Water content, %	Bromine		Total halogen (Cl)		Ratio Br/Cl $\times 10^3$	Equiatomic distribution Br/Cl $\times 10^3$
		Dry tissue, mg. %	Fresh tissue, mg. %	Dry tissue, %	Fresh tissue, %		
Case No. 3							
Blood	74.70	4.0	1.01	0.922	0.233	4.34	1.93
Heart	79.48	1.3	0.265	—	—	—	—
Liver	74.38	1.3	0.335	—	—	—	—
Lung	82.71	2.5	0.43	—	—	—	—
Spleen	76.46	1.9	0.445	—	—	—	—
Case No. 4							
Heart	78.41	1.5	0.325	—	—	—	—
Liver	77.31	1.6	0.365	—	—	—	—
Lung	79.50	3.5	0.715	—	—	—	—
Spleen	81.13	2.6	0.49	—	—	—	—
Case No. 5							
Bile (bladder)	91.71	4.0	0.33	—	—	—	—
Cerebellum	78.52	1.55	0.335	—	—	—	—
Cerebrum	77.69	0.2	0.045	—	—	—	—
Heart	78.86	0.3	0.065	—	—	—	—
Kidney	68.95	1.5	0.465	—	—	—	—
Liver	73.63	2.2	0.43	—	—	—	—
Lung	80.39	2.6	0.51	—	—	—	—
Medulla	75.00	1.1	0.275	—	—	—	—
Ovary	83.82	0.95	0.155	—	—	—	—
Pituitary	80.31	0.8	0.155	—	—	—	—
Spleen	78.44	2.7	0.58	—	—	—	—
Stomach	74.67	1.6	0.405	—	—	—	—
Uterus	80.92	1.4	0.265	—	—	—	—

*Lower half of medulla oblongata.

†Upper portion of medulla oblongata, including part of pons.

Discussion of Results

Among the values in the literature that appear to be too low, because of the use of unreliable methods (15), are those of Pribram (17) (no bromine in the brain, liver, pancreas and thyroid), Lobat (12) (no bromine in the liver, heart, spleen, kidney, blood serum; 0.015–0.02 mg. % in the cerebrum, and 0.07–3.0 mg. % in the thyroid), and Serbescu and Buttu (19) (no bromine in the liver, pancreas, heart, spleen, kidney, adrenal, pituitary, lung, muscle, and 0.415–3.15 mg. % in the thyroid). On the other hand Justus (9) analyzed 12 organs and found bromine present in each organ, the results varying from 14 to 122 mg. %; his method, undoubtedly, gave results that were too high.

Bernhardt and Ucko (1) published a long series of analyses, but, as Olszycka (16) has shown, these results are inaccurate and, therefore, cannot be considered for comparison.

With the exception of those of blood, few analyses based upon sound methods are available in the literature. These analyses are contrasted in Table II with the writer's analyses of the same tissues. Ucko's figures are included. His new method (21) has not been checked by other writers, and it may be open to the criticism made of the method of Bernhardt and Ucko (1). It will be seen that the figures are of the same order, but show wide variations. The variations are probably, in part, due to varying bromine intake (in diet and perhaps in medication) in the cases studied.

TABLE II
BROMINE CONTENT OF FRESH HUMAN TISSUES (VARIOUS WRITERS)

Tissue	Damiens (3)	Dixon (4)	Ucko (21)	Neufeld
	Mg. per 100 gm.			
Adrenal	—	—	0.33-0.66	0.22
Blood	0.52	0.28-1.64	0.15-0.35	0.62 -1.01
Kidney	0.25	—	0.27	0.335-0.82
Liver	0.18-0.37	—	0.17	0.04 -0.43
Lung	0.14-0.28	—	—	0.33 -0.715
Pituitary	—	0.42-2.39	—	0.12 -0.155
Spleen	—	—	0.24-0.33	0.225-0.58
Thyroid	—	—	0.48	1.78 -2.325

Bromine in blood. In addition to the figures recorded in Table II, the following apparently reliable values (in mg. %) have been published for individuals presumed normal, and not known to have been given bromine compounds therapeutically: Quastel and Yates (3 cases), 0.83-1.46 (18); Guillaumin and Merejkowsky (8 cases), 0.74-1.60 (6); Leipert (10 cases), 0.16-0.4 (10); and Ucko (100 cases), 0.15-0.35 (21).

Concerning the distribution of bromine between the corpuscles and plasma, Guillaumin and Merejkowsky (6) found the ratio "corpuscle Br to plasma Br" higher than the corresponding ratio for chlorine, while Hastings, Harkins and Liu (8) obtained a smaller value. Hastings and Van Dyke (7), and Leipert (10) found that normally there is a slight retention of bromine in the corpuscles, in agreement with the views of Böniger (2) on the permeability of the bromide ion. The bromide distribution between cells and plasma is not a constant value, but is dependent on the carbon dioxide content of blood, similar to chloride (Hastings and Van Dyke (7), and Leipert (10)).

Guillaumin and Merejkowsky (6) stated that 63 to 88% of the bromine is in organic combination; Ewer (5) found 55 to 78%; while Ucko (21) found only 20% of blood bromine in organic combination (he states that it is not in combination with plasma proteins). On the other hand, Yates (23) states

that all bromine in blood is in inorganic form. This latter work has been verified by Leipert (10) by means of deproteinization, dialysis and ultra-filtration, and this conclusion is almost certainly correct; the findings of Guillaumin and Merejkowsky, Ewer and Ucko must be rejected.

The results reported in this paper for normal blood are 0.62 to 1.01 mg. % (3 cases). The variation in bromine content is probably due mainly to differences in bromine intake.

Bromine in cerebrospinal fluid. The chlorine content of cerebrospinal fluid is always higher than that of blood plasma, in accordance with the Donnan equilibrium. Mishkis, Ritchie and Hastings (13) found that the concentration of bromine in the cerebrospinal fluid is always lower than the corresponding concentration in blood plasma. After the administration of bromide, Walter (22) observed a similar distribution. He found the ratio of "plasma Br to cerebrospinal fluid Br" normally to be 2.9-3.3. Leipert and Watzlawek (11) have obtained similar results, although they point out that this rather indicates a difference of permeability to anions, and not to bromide in particular.

Bromine in gastric juice. Nencki and Schoumov-Simanovsky (14) were the first to show that when bromide is administered it replaces part of the chloride in the gastric juice. Quastel and Yates (18) found a drop of 25 to 30% of bromine in the blood following a meal. Leipert (10) has obtained similar results. The actual contents of gastric juice in his four analyses were 0.312 to 1.226 mg. %, each one higher than the corresponding blood bromine. Ucko (21) found the value to be 0.5 to 0.9 mg. per 100 cc. in gastric juice from the "fasting" stomach.

Bromine in urine. The excretion of bromine in urine in absence of specified bromine administration has been determined by a number of writers. Leipert (10) found this value to be 3 to 5 mg. per 24 hr., and Ucko (21), 1.0 to 2.5 mg. Both writers and also Hastings, Harkins and Liu (8) state that the ratio "bromine to chlorine" is always slightly lower in urine than in blood.

Bromine in the pituitary. The assumption that the function of the pituitary is important in bromine metabolism, as set out by a number of writers (reviewed in Part I of this series), has not received any confirmation in the more accurate work of Dixon (4). The results obtained by the writer (in Parts I and II of this series) are in full agreement with those of Dixon.

Bromine in the thyroid. In the first paper of this series the results appeared to indicate that the thyroid stored amounts of bromine definitely greater than could be ascribed to blood circulating through the different tissues. Results in this paper also appear to suggest that this is the case. In addition the writer analyzed certain thyroid material obtained from the operating theatre at partial thyroidectomy. The results obtained for bromine, iodine, and total halogen are shown in Table III in mg. %. All the operative cases had been treated with Lugol's solution prior to operation.

TABLE III
ANALYSES OF HUMAN THYROID MATERIAL (mg. %)

	Water	Bromine		Iodine		Total halogen		Equiatomic distribution Br : I : Cl
		Dry tissue	Fresh tissue	Dry tissue	Fresh tissue	Dry tissue	Fresh tissue	
Normal	76.74	10.1	2.33	169.0	39.3	678.5	157.8	1 : 10.6 : 141.2
Normal	77.77	8.1	1.78	107.0	23.8	660.0	146.8	1 : 8.4 : 176.2
Graves' disease	81.94	50.3	9.08	264.5	47.8	752.5	135.9	1 : 3.3 : 29.5
Graves' disease	86.30	12.45	1.71	186.5	25.6	760.5	104.2	1 : 9.6 : 127.0
Graves' disease long standing	87.97	6.8	0.82	83.0	10.0	597.0	71.8	1 : 8.0 : 188.6
Pressure symptoms non- toxic goitre	82.58	13.05	2.28	43.5	7.6	4157.0	724.0	1 : 2.1 : 713.2

The results in Table III show variations in the ratios of the three halogens that are too great to permit any conclusions to be drawn beyond the fact that in the thyroid the ratio of bromine to chlorine is greater than that in other tissues. This, perhaps, supports the view that bromine is concerned with thyroid metabolism, although the writer (15) could find no evidence that bromine is associated with the functioning compound, thyroglobulin, of the thyroid. Nevertheless, all the findings recorded in this and in the previous paper suggest that a more detailed study of thyroid material may reveal some functional significance for bromine in this gland; it is hoped to carry out such a study at a later date.

Bromine to chlorine ratio. Earlier figures for human and other mammalian tissues (weight-ratios) are summarized and given in Table IV (all $\times 10^3$).

TABLE IV
THE BROMINE TO CHLORINE RATIO IN MAMMALIAN TISSUES

	Ucko (21)	Leipert (10)	Damiens (3)	Neufeld
Organs (not including thyroid)	1.5-8.0	-	0.21-4.53	1.19-5.86
Gastric juice	1.7-5.5	1.54-3.98	-	-
Blood	0.5-1.4	0.62-1.42	1.32-1.55	2.34-4.34
Urine	0.3-0.6	0.41-0.57	0.39-1.85	-

These figures, and the detailed figures in Table I do not show sufficient constancy to suggest that any physiological ratio exists. The figures in Table I suggest that the ratio for the thyroid is relatively much greater than for other tissues, but these are based on only two analyses, while Ucko (21) did not, in his analyses, find such high ratios. This finding, therefore, cannot be stressed until a larger number of analyses have been made.

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